Supporting information

NMR experimental: Bruker Avance-300, Avance-400, Avance-500 and Avance-600 were used for solution NMR analysis. ¹H NMR DOSY measurements were performed at 500.13 MHz with a 5 mm ¹H/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. ¹H NMR DOSY measurements were performed at 500.13 MHz with a 5 mm ¹H/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 MoKa radiation. The structures were solved using SHELXS-97 and refined by full matrix leastsquares 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(OPrⁱ)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 Ti₂(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 $\text{Ti}(\text{OPr}^{i})_{4}$ (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 $\text{Ti}_2(\text{cat})_4(\text{DMA})_2$ 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 $\text{C}_{32}\text{H}_{34}\text{O}_{10}\text{Ti}_2\text{N}_2$ (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 CHCl₃ was mixed with a solution of $Ti_{10}O_{12}(cat)_8(py)_8$ (5 mg) in CHCl₃. The desired product was obtained by slow diffusion of diethyl ether into the mixture. The crystalline precipitate was filtered and dried under vacuum. ¹³C 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) Ph<u>py</u>), 148.8 (C (4) Ph<u>py</u>), 137.2 (C (1) <u>Ph</u>py), 129.0 (C-H (3, 4, 5) <u>Ph</u>py), 126.9 (C-H (2, 6)<u>Ph</u>py), 121.3 (C-H (3, 5) Ph<u>py</u>), 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 $C_{136}H_{104}N_8O_{28}Ti_{10}$, CHCl₃ (MW 2896.37): C 56.81; H 3.65; N 3.87. Found C 56.37; H 4.05; N 4.00.

S H A P Electronic St	E v2.1 tructure G	Continu roup, Univ	uous Shape Measures calculation (c) 2013 versitat de Barcelona Contact: llunell@ub.edu		
D6h	Hexagon				
C5v	Pentagonal pyramid				
Oh	Octahedron				
D3h	Trigonal prism				
C5v	Johnson pentagonal pyramid J2				
		1 0			
PPY-6	OC-6	TPR-6	JPPY-6		
22.189,	2.016,	11.278,	25.704		
PPY-6	OC-6	TPR-6	JPPY-6		
24.934,	1.430,	13.562,	28.296		
PPY-6	OC-6	TPR-6	JPPY-6		
25.204,	1.321,	11.724,	29.093		
	S H A P Electronic Si D6h C5v Oh D3h C5v PPY-6 22.189, PPY-6 24.934, PPY-6 25.204,	S H A P E v2.1 Electronic Structure G D6h Hexago C5v Pentago Oh Octahed D3h Trigona C5v Johnson PPY-6 OC-6 22.189, 2.016, PPY-6 OC-6 24.934, 1.430, PPY-6 OC-6 25.204, 1.321,	S H A P Ev2.1ContinElectronic Structure Group, UnivD6hC5vPentagonal pyramiOhOctahedronD3hTrigonal prismC5vJohnson pentagonaPPY-622.189,2.016,11.278,PPY-6OC-6TPR-624.934,1.430,13.562,PPY-6OC-6TPR-625.204,1.321,11.724,		



Figure 1: ¹H NMR spectra of $[Ti_{10}O_{12}(cat)_8(py)_8]$ (CD₂Cl₂, 500 MHz)



Figure 2: ¹³C NMR spectra of $[Ti_{10}O_{12}(cat)_8(py)_8]$ (CD₂Cl₂, 125 MHz)



Figure 3: ¹³C NMR spectra of $[Ti_{10}O_{12}(cat)_8(py)_8]$ (CDCl₃, 125 MHz)



Figure 4: ${}^{13}C$ NMR spectra of $[Ti_{10}O_{12}(cat)_8(py)_8]$ (DMSO, 125 MHz)



Figure 5: ¹³C NMR spectrum of the compound which crystallized after dissolution of the $[Ti_{10}O_{12}(cat)_8(4,4'-bipy)_x]_{\infty}$ precipitate in pyridine (CDCl₃, 125MHz). The $[Ti_{10}O_{12}(cat)_8(4,4'-bipy)_x]_{\infty}$ precipitate was obtained by mixing $[Ti_{10}O_{12}(cat)_8(py)_8]$ and 4,4'-bipyridine in CHCl₃. This spectrum is identical as the one recorded for $[Ti_{10}O_{12}(cat)_8(py)_8]$.



Figure 6: ¹³C NMR spectrum of crystals obtained by reaction between $Ti_2(cat)_4(DMA)_2$ and pyridine without addition of water (CDCl₃, 125 MHz)



Figure 7: ¹³C NMR spectra of crystals obtained by reaction between $Ti_2(cat)_4(DMA)_2$ and pyridine with addition of water (10 μ L) (CDCl₃, 125 MHz)



Figure 8: ¹³C 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 (CD₂Cl₂, 125 MHz)



Figure 9: Powder X-Ray Diffraction patterns of $[Ti_{10}O_{12}(cat)_8(py)_8]$ obtained after dissolving the $[Ti_{10}O_{12}(cat)_8(4,4'-bipy)_x]_{\infty}$ 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 $[Ti_{10}O_{12}(cat)_8(py)_8] \bullet (py)_6$ in CH_2Cl_2 , $c = 10^{-5}$ mol.l⁻¹.

Weight of	Volume	Volume of water (µL)	Weight of
$Ti_2(cat)_4(DMA)_2$	of		$[Ti_{10}O_{12}(cat)_8(py)_8]$
(mg)	pyridine		crystals (mg)
	(mL)		
100	7.5	0	33
100	7.5	6	14
100	7.5	10	6
100	7.5	20	1
100	7.5	30	No crystals
100	7.5	40	No crystals

Table 1: Synthesis of $[Ti_{10}O_{12}(cat)_8(py)_8]$ performed with an increasing amount of water



Figure 12: Thermogravimetric analysis of $[Ti_{10}O_{12}(cat)_8(py)_8]$: 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 $[Ti_{10}O_{12}(cat)_8(py)_8] \bullet (py)_4$ 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]