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Hybrid porous titania phosphonate networks with different bridging

# 2 functionalities: synthesis, characterization, and evaluation as efficient solvent separation materials

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# Abstract

- 14 Hybrid titania phosphonate materials can demonstrate a high added value as tailored sorption materials. They combine high chemical stability with great structural versatility, given the wide
- 16 diversity of functional groups that can be incorporated. Hereto, a fundamental understanding of the synthesis strategies influencing the material performance is required. Therefore three porous TiO<sub>2</sub>
- 18 phosphonate hybrid structures with different functional groups (octyl, propyl, and phenyl) were evaluated in a solid-phase extraction application aimed towards solvent separation. The synthesis
- 20 was performed by mixing bridged diphosphonic acids (DPAs) with Ti(OBu)₄ in a water-ethanol mixture at 30°C, followed by a hydrothermal post-treatment at 120°C. The materials were
- 22 characterized by ICP-AES, <sup>31</sup>P solid-state CP/MAS NMR, Raman and FTIR spectroscopy, X-ray diffraction, N<sub>2</sub>-sorption, and transmission electron microscopy. It is shown that the diphosphonic
- 24 acids are quantitatively incorporated in the hybrid structures, leading to nanosized particles with a complex but uniquely functionalized surface. A study of the pore structure as a function of the
- 26 incorporated DPA amount showed materials with a maximum BET surface area of 379 m<sup>2</sup>/g. The alkyl functionalized hybrid titania phosphonates demonstrated excellent and tunable sorption behavior.
- 28 Keywords: Hybrid porous titania organophosphonates, Hydrothermal synthesis, <sup>31</sup>P solid-state NMR, SPE for solvent separation.

30 1. Introduction

The extensive versatility and unique associated properties of porous organic-inorganic hybrid

- 32 materials have instigated impressive research efforts in this scientific domain. The flexibility of combining functional inorganic scaffolds with the incorporation of tailored organic functional groups
- 34 and spacers opens up the possibility to simultaneously design both the bulk matrix structure and interfacial properties to match a specific target application. This makes hybrid materials very suitable
- 36 for applications such as sorption, separation, ion exchange, and heterogeneous catalysis [1-7].

However, material stability plays a vital role in allowing the agile transfer of these designed materials

- 38 from an academic environment to higher technology readiness levels (TRL levels). Indeed, industrial processes are often performed in large-scale reactors under harsh chemical environments which
- 40 require both chemical and mechanical robustness. The stability of hybrid materials is dependent on the inorganic scaffold, the incorporated organic functionalities, and the anchoring mechanism
- 42 between both. In this context, the combination of a tetravalent metal ion M(IV) with a phosphonate coupling molecule is particularly interesting, as they tend to form M(IV)-O-P bonds with
- extraordinary chemical stability, rendering them insoluble, even in highly acidic media below pH 1.This enables the metal phosphonate structures to withstand extreme conditions, such as the acidic
- 46 media used to separate lanthanides and actinides from nuclear waste [8-11]. The stability could also lead to facile recuperation if the material is used in separation processes. However, this inherent
- 48 stability comes with the downside of rapid condensation reactions during the synthesis, leading to daunting challenges in controlling the reaction conditions and reproducing the resulting structures in
- 50 sol-gel-based synthesis approaches. The fast kinetics of the heterocondensation between the metal(IV) precursors and the diphosphonic acids ultimately complicates the formation of a controlled
- 52 porosity [12]. In addition, the ligating modes of the diphosphonic acids and their impact on the hybrid structure are still poorly understood.

- 54 Nonetheless, numerous metal phosphonate systems based on tetravalent metals have been synthesized. Zirconium (IV) [13-16], titanium (IV) [17-20], and tin (IV) [8, 21] organophosphonates
- 56 with a wide variety of different organic functional groups have been reported in literature. These studies often focus on the separation applications of metal ions, such as lanthanides from solutions.
- 58 The reported materials utilize available, non-condensed POH groups [14, 15] or focus on the incorporation of amine groups [19, 22] to optimize sorption capacities. While several types of hybrid
- 60 materials have been tested for their capability to separate aromatic compounds [1, 23, 24], the incorporation of alkyl bridging groups, their impact on the hydrophobicity and porosity of the
- 62 materials, and consequently their separation capability have been rarely reported, resulting in a lack of knowledge regarding the synthesis-properties-sorption behavior of these materials [25].
- 64 This lack of information regarding the separation capabilities might be due to the observation that metal phosphonate networks usually form dense layered structures with limited porosity, which
- 66 limits the efficient diffusion of organic compounds [3, 12]. While multiple methods have been deployed to introduce (meso)porosity in these hybrid structures [12], one of the most frequently
- 68 used is a template-based method where a surfactant is incorporated to control pore size and volume [25, 26]. However, the inclusion of organophosphonates makes the subsequent surfactant removal
- by thermal treatment exceptionally difficult due to possible joint degradation of the hybrid structure.
   Solvent extractions are a possible alternative but are often associated with lengthy, labor- and
- solvent-intensive protocols [27]. The use of a template-free method, however, has also been provento be efficient [28]. In a very recent study, Wang *et al.* [29] also illustrated the formation of a hybrid
- 74 titania-organophosphonate with tunable porosity via a non-hydrolytic sol-gel synthesis without templating surfactants by using rigid bis-diethylphosphonate precursors.
- 76 In the present work, a surfactant-free hydrothermal synthesis method towards hybrid porous titanium organophosphonates is described by employing diphosphonic acids containing different
- 78 spacer groups (1,3-propyl, 1,8-octyl, and 1,4-phenyldiphosphonic acid). The choice for different

spacer groups aims to introduce control over the hydrophobicity which can impact the separation

- 80 properties in extraction applications. It is shown that careful optimization of the synthesis conditions allows quantitative incorporation of the aimed titanium/diphosphonic acid ratio. The presented
- 82 hybrid materials are characterized in depth using ICP-AES, <sup>31</sup>P solid-state NMR, Raman spectroscopy, TEM, XRD, and N<sub>2</sub> sorption as complementary techniques in order to evaluate the complex and
- 84 fundamental synthesis/structure/properties relationships. In addition, the sorption behavior of the materials is assessed in a solid phase extraction (SPE) application, demonstrating that its
- 86 performance can surpass this of commercially available grafted silica products.

#### 2. Experimental

#### 88 2.1 Materials and Methods

Tetrabutylorthotitanate (TBT, ignition residue 23,5%), 1,3-propyldiphosphonic acid (PrDPA, >98%)

- 90 and 1,4-phenyldiphosphonic acid (PhDPA, >98%) were purchased from TCI chemicals. 1,8octyldiphosphonic acid (ODPA, 97%) was purchased from Merck. These chemicals were stored in a
- 92 desiccator and used without further purification. The desiccator containing the DPAs was stored at 4°C. Absolute ethanol (>99.95%) AnalaR Normapur<sup>®</sup> and HCl (37%) AnalaR Normapur<sup>®</sup> were
- 94 purchased from VWR. The digestion prior to the elemental analysis was performed using Merck suprapur<sup>®</sup> 40% HF and Baker Instra-Analyzed<sup>®</sup> reagent 69% HNO<sub>3</sub>. The SPE tests were performed
- 96 with MilliQ water (18.1 MΩ cm<sup>-1</sup>), methanol (≥99.8% AnalaR NORMAPUR<sup>®</sup>, ACS), MeOH-d₄ (≥99.8 atom% D, Aldrich), n-heptane (≥99%, EMSURE<sup>®</sup> Reag. Ph Eur), and pyridine (≥99%, GPR RECTAPUR<sup>®</sup>).
- 98 Synthesis of the hybrid titania. All reactions are performed under standard atmosphere. An acidic stock solution of water and ethanol was prepared by stirring 50 g MilliQ water, 3.75 g HCl (37%) and
- 100 13.1 g ethanol. This stock solution was prepared daily. Then, the appropriate amount of diphosphonic acid (DPA) was added to 20 ml of this stock solution to obtain Ti/2P atom ratios (feed
- 102 ratios) between 1 and 20 (this is half the molar ratio of TBT to DPA, as every DPA contains two phosphorus atoms). Afterward, 1.5 g (4 mmol) of TBT (Ti(OBu)<sub>4</sub>) was added to the reaction mixture

- under vigorous stirring at a controlled rate of 2 g/min using a peristaltic pump (VWR, PP3300). This results in a molar ratio of 188/18.5/2.5/1 for H<sub>2</sub>O/EtOH/HCl/TBT, respectively. This mixture was
- 106 allowed to stir at 30 °C for 24h in a closed vessel before being transferred to a 125 ml hydrothermal bomb (Parr, model 4748), in which it was heated to 120 °C for 24 hours without stirring. The resulting
- solids with a Ti/2P ratio between 1 and 5 were filtered off using Whatman<sup>®</sup>40 filter paper on a büchner set-up. The samples with a Ti/2P ratio of 10 and 20 and the sample without DPA were
- filtered on a Pall Supor<sup>®</sup> 0.1 μm membrane on a büchner set-up. A different filter was used to avoid filter clogging of the high phosphorus content materials. All samples were washed with 200 ml of
- 112 MilliQ water before drying under vacuum at room temperature. The resulting flakes were powdered using a pestle and mortar and stored in a desiccator filled with silica beads in the dark until further
- analysis. A schematic overview of the synthesis procedure can be found in Figure 1. The materials are labeled TiO<sub>2</sub>-X-Y, where X is C3 for propyl, C8 for octyl, and Ph for the phenyl-modified samples. Y
- 116 represents the atom ratio (Ti/2P) in the feed ratio.

#### 2.2 Chemical composition analysis

- 118 A microwave acid digestion of the hybrid titania powders was performed in a Milestone Ethos reactor by adding 20-30 mg of sample to 7.5 ml of HNO<sub>3</sub> and 2.5 ml of HF in a Teflon vessel and
- ramping the temperature to 220°C in 20 min, at which the sample was held isothermally for another
   15 min. The resulting mixtures were allowed to cool to room temperature before being transferred
- 122 in 250 ml polypropylene flasks and diluted with MilliQ water. The mixtures were then analysed on an Optima 8300 DV ICP-AES instrument (PerkinElmer, Waltham, USA) in axial view mode. Instrument
- 124 calibration was done using the Merck titanium standard reference Certipur<sup>®</sup> and VWR Chemical Phosphorus Plasma Emission Standard dilutions between 0.01 and 100 mg/l. Samples were
- measured once, and error propagation was used to calculate the deviation on the Ti/2P ratios found.

#### 2.3 Hybrid structure analysis

- 128 Phosphorus-31 solid-state CP/MAS (cross-polarization magic angle spinning) NMR spectra were acquired at ambient temperature on an Agilent VNMRS DirectDrive 400 MHz spectrometer (9.4 T
- 130 wide-bore magnet) equipped with a T3HX 3.2 mm VT probe dedicated for small sample volumes and high decoupling powers. Magic angle spinning (MAS) was performed at 15 kHz using ceramic zirconia
- rotors of 3.2 mm in diameter (22  $\mu$ L rotors). The phosphorus chemical shift scale was calibrated with orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) at 0 ppm. Other acquisition parameters used were: a spectral width of
- 134 50 kHz, a 90° pulse length of 2.5  $\mu$ s, a spin-lock field for CP of 80 kHz, a contact time for CP of 0.9 ms, an acquisition time of 15 ms, a recycle delay time of 8 s and 100-200 accumulations. High power
- 136 proton dipolar decoupling during the acquisition time was set at 60 kHz. The Hartmann-Hahn condition for CP was calibrated accurately on the samples themselves. The X-ray diffraction (XRD)
- analysis was done using a Bruker D8 diffractometer with Cu-K $\alpha$  X-rays of wavelength ( $\lambda$ )=1.5406 Å. The diffractograms were measured in the range of 10° to 60° in steps of 0.040°. The morphology of
- 140 the powders was studied with transmission electron microscopy (TEM) on a FEI Tecnai Spirit TEM operating at 120 kV . The local element composition was determined with energy dispersive X-ray
- 142 (EDX) analysis. Raman spectroscopy was performed with a Horiba Jobin Yvon T64000 triple Raman spectrometer equipped with a BXFM Olympus microscope (100x magnification objective), a Horiba
- 144 Jobin Yvon Sym-phony CCD detector and a 488 nm Lexel SHG laser operating at approximately 400 mW and a spot size diameter of  $2.381 \,\mu$ m. The confocal hole diameter was minimized to improve the
- 146 spatial resolution. The specific surface area  $(S_{Bet})$  of the hybrid powders was estimated by using the Brunauer-Emmett-Teller (BET) theory applied on the N<sub>2</sub> physisorption isotherms (Micromeritics,
- 148 Tristar II). Samples were flushed with nitrogen at 150°C for 16 h prior to the measurement in order to remove any residual adsorbed components. The pore size distribution was estimated by a NL-DFT
- 150 method with the "cylindrical pores in pillared clay" kernel of Micromeritics. The relative pressure range of the N<sub>2</sub> adsorption isotherm was set from 0.001 to 0.9 with a regularization, i.e. smoothing,

152 set at 0.1.

Hybrid materials were dried at 50°C overnight in a vacuum oven (100 mbar) before packing SPE

- 154 cartridges with 500 mg between two plugs. The columns were then activated subsequently with 2 ml of  $H_2O$  and 1 ml of deuterated MeOH. The columns were then loaded accordingly to the functional
- 156 group present: the TiO<sub>2</sub>-C8 and TiO<sub>2</sub>-C3 columns with 3 ml of a 4/1 (v/v) MeOH/heptane mixture, while the TiO<sub>2</sub>-Ph columns were loaded with a 4/1 (v/v) MeOH/pyridine mixture. The eluate was
- 158 collected and measured with <sup>1</sup>H NMR to determine the residual heptane and pyridine in the filtrates.
   The results obtained with the TiO<sub>2</sub>-C8, TiO<sub>2</sub>-C3, and TiO<sub>2</sub>-Ph materials were compared with
- 160 commercial 500 mg C8 (BAKERBOND<sup>™</sup> SPE Octyl) and phenyl (BAKERBOND<sup>™</sup> SPE Phenyl) SPE columns, respectively.
- 162 The remaining amount of heptane in the eluates after SPE over the TiO<sub>2</sub>-alkyl SPE columns was calculated using the <sup>1</sup>H-NMR integration values of both the eluate and the 4/1 v/v (17/1 molar ratio)
- 164 MeOH/heptane start mixture (reference) and the following formula:

# $\frac{\#Mole_{MeOH, eluate}}{\#Mole_{Heptane, eluate}} / \frac{\#Mole_{MeOH, reference}}{\#Mole_{Heptane, reference}} *100\%$

For MeOH, only the hydrogens of the CH<sub>3</sub> group were taken into account, while for heptane both the CH<sub>3</sub> and CH<sub>2</sub> groups were taken into account. A similar formula was used for the phenyl materials,
with pyridine replacing heptane.

#### 3. Results and discussion

#### 170 **3.1 Composition of the porous titania diphosphonate networks**

In order to demonstrate the successful incorporation of the organodiphosphonic acids, the hybrid

- 172 networks were analyzed with ICP-AES (Table 1). Excellent agreement is observed between the synthesis feed ratios and the obtained ratios, indicating a quantitative incorporation of the DPA in
- the  $TiO_2$  matrix. Almost all samples have a slight increase in their actual Ti/2P ratios as compared to the feed ratio used, indicating that a tiny fraction of (unreacted) linker is lost during the washing
- 176 steps of the hybrid structures.

Together with the porosity, the tunable amount of incorporated diphosphonic acid is an important

- 178 parameter since it determines the adsorptive characteristics in sorption applications. The straightforward scaling of the effective diphosphonic acid incorporation with the feed ratio allows to
- 180 establish straightforward correlations with the resulting physicochemical properties. The quantitative incorporation of the diphosphonic acids makes these hybrid materials also highly sustainable as
- 182 compared to the widespread method for producing hybrid materials, i.e., grafting for which an excess of (di)phosphonic acid is used [30, 31], resulting in a less favorable atom economy.

#### 184 **3.2 Structural properties of porous titania diphosphonates**

Given the quantitative incorporation of the DPAs, the next important step is to explore the

- 186 underlying hybrid structures in terms of stability, phosphonic acid binding mode, (anatase) crystal formation and grain size distribution. The thermal stability of the materials was briefly tested in a
- 188 TGA experiment. It was found that the least stable organic group is the octyl chain from TiO<sub>2</sub>-C8, which starts deteriorating at 328°C, followed by the propyl chain from TiO<sub>2</sub>-C3, which starts
- 190 deteriorating at 420°C. Ultimately the most thermally resistant material is the hybrid  $TiO_2$ -Ph, which only shows signs of thermal oxidative degradation starting from 553°C (SI, Figure S1). Phosphorus
- 192 NMR (<sup>31</sup>P-NMR) is a widespread tool to analyse the binding modes of phosphonates on metal oxide surfaces as the coordination of the organophosphonic moiety will change the chemical shift and
- 194 bandwidth of the observed peaks. The NMR signal characteristics of phosphorus nuclei that are covalently coupled to the titania via P-O-Ti condensation bonds are subject to i) an upfield shift upon
- 196 formation of a covalent Ti-O-P bond and ii) severe peak broadening arising from slightly different chemical environments around the phosphorus nucleus as a result of a multitude of weak H-bond
- 198 interactions of the remaining P-OH and P=O groups with surface OH groups, neighboring POH or P=O groups, and even trapped water [30], and iii) further peak broadening due to hindered mobility of
- 200 the diphosphonate linkers caused by steric constraints. It is generally accepted that there are mono-, bi- and tridentate Ti-O-P binding modes for which the <sup>31</sup>P-NMR peaks appear in a rather small

- 202 chemical shift window of the spectrum (roughly between -10 and 40 ppm) and partly overlap [30, 32, 33]. The appearance of broadened and overlapping <sup>31</sup>P-NMR signals is also observed for all hybrid
   204 materials presented in this study (Figure 2), confirming the strong covalent coupling between the diphosphonic acids and the titania.
- 206 For the TiO<sub>2</sub>-C8 hybrids prepared with a low feed ratio (Figure 2), broad signals appear upfield (around 25 ppm and 15 ppm) and downfield (around 34 ppm) compared to the signal of pure ODPA
- 208 (C8-pure) at 30.5 ppm, confirming the condensation of the octyldiphosphonic acid. The cause of the broad peak lineshapes is explained above. Eye-catching is the TiO<sub>2</sub>-C8-1 material showing an
- 210 extensively upfield shifted peak around 8 ppm signifying a unique structural feature. This dominant P-environment in the  $TiO_2$ -C8-1 material that quickly disappears at higher feed ratios could be
- 212 attributed to the presence of layered structures as indicated by TEM images (Figure 3a) and backed by earlier observations that high concentrations of long alkyl chains lead to the formation of layered
- 214 structures [4, 12]. Additionally different categories of particles fluctuating in size (Figure 3) and Ti/Pcomposition are supported by TEM (EDX spectra can be found in the SI, Figures S2 and S3). The
- 216 layered structures are not observed in the  $TiO_2$ -C3 hybrids for which no peak is observed below 10 ppm regardless of the Ti/2P ratio (Figure 2b), which might be due to the absence of structuring van
- der Waals interactions between the short propyl chains. Upon increasing the feed ratio for the TiO<sub>2</sub> C8 hybrids, the broad signals gradually evolve downfield towards somewhat more distinct and
- sharper signals, pointing to more similar phosphorus environments with higher mobility due to reduced sterical constraints. For the  $TiO_2$ -C8-20 hybrid with the highest feed ratio, the <sup>31</sup>P-NMR
- 222 spectrum shows four relatively distinct peaks around 34 ppm, 30 ppm, 28 ppm and 21 ppm. This is in contrast with bridged titania-diphosphonate networks showing a single broad peak between 40 and

5 ppm allocated to completely condensed diphosphonic acid groups [29].

A complete assignment of all the NMR signals is non-trivial. Recent models based on the grafting of PAs on a titania surface have shown that a bidentate binding leads to a downfield shift compared to

the free PA, while upfield shifts have been allocated to monodentate binding modes [34, 35].

- 228 Alternatively, it has been suggested that each condensation between a P-OH group and Ti-OH group leads to an upfield shift, but that interactions between the P=O groups and surface Lewis or Brønsted
- acidic sites lead to downfield shifts [32, 36]. In general, both models indicate a more downfield shift for a more intimate binding between the phosphonic acid and the inorganic scaffold, leaving fewer
- 232 'dangling' phosphonic acid functionalities, which can be supported in this study by the relative excess of titania under the high feed ratio conditions. The binding can also be observed in IR and Raman (SI,
- Figure S4 and S5). Lowering the Ti/2P ratio leads to an excess of DPA as well as increased sterical hindrance between the chains of bonded DPA, resulting in more monodentate bonds and therefore
- 236 upfield peak shifting. It should also be taken into consideration that the structures studied in this study are not obtained by grafting, meaning that the titania facets at the interface between the DPA
- 238 and titania do not necessarily represent the ordered anatase structure supposed in the modelling studies. The (partly) amorphous nature of the synthesized hybrids is indicated by the lack of electron
- 240 diffraction patterns in TEM for particles high in phosphorus content (SI, Figure S6).

A similar trend is observed for the 10 to 40 ppm region of the TiO<sub>2</sub>-C3 materials (Figure 2b). The pure

- 242 PrDPA (C3-Pure) displays three chemical shifts around 37, 36, and 32,5 ppm. At low feed ratios these signals merge into a broad signal around 26 ppm, accompanied by downfield and upfield shoulders
- 244 around 34 and 18 ppm respectively. Also here, the broadness of the signals is the result of a collection of slightly different phosphorus chemical environments and reduced chain mobilities due
- 246 to steric constraints in the disordered structures. The overall upfield shift compared to the pure PrDPA is similar as for  $TiO_2$ -C8. No indications for layered structures are present. As for the  $TiO_2$ -C8
- 248 materials, the broad 26 ppm peak evolves downfield towards more distinct and sharper signals upon increasing the feed ratio, pointing to more similar phosphorus environments and higher mobilities of
- 250 the DPA chains due to reduced constraints. In other words, an incorporation of less diphosphonic acids results in more defined chemical environments. The similarities between the TiO<sub>2</sub>-C8 and TiO<sub>2</sub>-
- 252 C3 spectra imply that the surface interactions and condensations are independent of the length of

the DPA alkyl chain, while their relative occurrence can differ somewhat. This may have several

- 254 causes, like variations in the reaction rates of the concurrent Ti-O-P hydrolysis/condensation reactions and/or changes in van der Waals forces depending on the length of the PA chain, leading to
- 256 different interactions between the organic chains and thus variations in the binding modii. In addition, other effects like differences in solubility and hydrophobicity can not be excluded and
- 258 further research is needed to fully understand these relationships.

The signals of the TiO<sub>2</sub>-Ph materials appear in a smaller region between 0 to 20 ppm (Figure 2c), and

- 260 compared to the  $TiO_2$ -alkyl materials, clearly fewer signals are observed. This can be attributed to the inherent stiffness of the phenyl group versus the relatively flexible alkyl chains, resulting in more
- 262 similar phosphorus environments due to  $\pi$ - $\pi$  stacking between the aromatic rings of the diphosphonic acid groups [7, 37] or stabilizing  $\pi$ -H interactions between the aromatic rings and water
- 264 [38, 39]. The <sup>31</sup>P-NMR spectrum of pure PhDPA (Ph-Pure) shows a single peak at 15.8 ppm. For low feed ratios, mainly three signals are observed around 5 ppm, 12.3 ppm, and a downfield shoulder
- around 15 ppm. This is consistent with signals observed for other phenyl-modified titania [31, 40].For the higher feed ratios, only the signals at 12 and 15 ppm remain.
- 268 Subsequently, crystallinity is an essential structural indicator as it can e.g. influence stability, catalysis mechanisms, porosity, and the available surface area sites which can in turn influence sorption
- 270 interactions. Both Raman spectra and XRD patterns (Figure 4) display the formation of anatase particles in all samples, albeit a very limited amount for the lowest feed ratio. Starting from a feed
- 272 ratio of three, pronounced signals appear at 152, 400, 499 and 648 cm<sup>-1</sup> which can be allocated to the E<sub>g</sub>; B<sub>1g</sub>; A<sub>1g</sub> and B<sub>1g</sub>; and E<sub>g</sub> lattice vibrations of anatase titania, respectively [41, 42]. These are
- 274 matched by X-ray reflections at 25°, 38°, 48° and 54°, supporting the formation of anatase particles
  [43]. Hence, it can be concluded that excessive incorporation of diphosphonic acids (small Ti/2P
  276 ratios) inhibits the formation of crystalline anatase domains.
  - 11

While the formation of anatase crystals is evident as soon as TBT is present in surplus, both TiO<sub>2</sub>-Ph-1

- and TiO<sub>2</sub>-C8-1 already show some minor presence of the  $E_g$  anatase peak (152 cm<sup>-1</sup>) and the (101) diffraction peak of anatase at 25°. The clear presence of anatase signals in both the XRD
- 280 diffractogram and the Raman spectrum of TiO<sub>2</sub>-Ph-1 might indicate that the condensation reaction between phenyldiphosphonic acid and TBT is slower compared to the reaction between ODPA or
- 282 PrDPA and TBT, resulting in a larger amount of anatase formation, even when equivalent Ti/2P reaction ratios are used. Additionally, the XRD patterns show weak reflections at 27°, 36°, and 41°,
- 284 pointing to a small amount of rutile phase in all  $TiO_2$ -Ph materials and to a somewhat lesser extent for the alkyl-TiO<sub>2</sub> materials for which mainly the 27° peak is observed as a shoulder of the 25° peak.
- As such, it can be concluded that the phenyl groups impose a slight alternative ordering of the hybrid material, facilitating the formation of a small amount of rutile in the inorganic scaffold. The peak at
- 288 22° in the diffractogram of  $TiO_2$ -C8-1 (Figure 4a) could possibly be assigned to stacked octyl chains within a layered structure [44]. The unassigned sharp peak at 13° in the same sample could be
- 290 related to a yet unidentified ordering in hybrid phosphonates however a specific structure could not be determined due to a lack of single crystal formation (SI, figure S7). The additional peak at 32° for

TiO<sub>2</sub>-Ph-1 (Figure 4e) probably indicates brookite formation [45, 46].

It should be noted that the  $E_g$  peak in the Raman spectra of all samples showing anatase signals is

- 294 blue-shifted between 151 and 157 cm<sup>-1</sup> compared to the usual location at 144 cm<sup>-1</sup> (Table S2). A blue shift of the  $E_g$  peak has been linked to the formation of small (<10 nm) nanoparticles of anatase and
- 296 the corresponding phonon confinement effect [47-49]. The blue shift is independent of the feed ratio, implying that the size of the nanoparticles remains similar for a wide range of feed ratios. This
- is in agreement with the peak broadening in XRD, being also an indication for nanoparticle formation[50, 51]. The qualitative observation of similar peak widths in XRD confirms the independence of the
- 300 crystal size on the feed ratio. Furthermore, the TEM images of TiO<sub>2</sub>-C8-1 show clusters of 4 nm-size nanoparticles (Figure 3b).

- 302 To summarize, both the type and feed ratio of the diphosphonic acid determine the structure of the hybrid material, resulting in a general inhibition of  $TiO_2$  crystal growth at high diphosphonic acid
- 304 contents due to the formation of strong Ti-O-P bonds, and with the supplementary formation of a distinct layered structure in case of the octyl spacer. In addition, both the P-O-Ti binding modes
- 306 (NMR) and amount of anatase crystal formation of the inorganic scaffold are systematically affected by the Ti/2P ratio, allowing to conclude that the diphosphonic acids are structure-determining
- 308 components of the hybrid titanium phosphonates, besides their expected capability to change the hydrophobicity of the hybrid structures.

### 310 **3.3 Revealing the underlying structural properties of porous metal diphosphonates**

A change in the Ti/2P ratio has, as shown above, a clear influence on the resulting hybrid structure

- 312 (Ti-O-P binding modes; weak H-bond interactions formed...). The porosity arising from the assembly of nanoparticles and organic spacers in the titania matrix is also an important parameter to assess in
- 314 view of the target applications. The N<sub>2</sub> sorption isotherms (Figure 5) show that the introduction of alkyl-based diphosphonic acids leads to a remarkable feed ratio-dependent effect on the isotherms.
- 316 Low feed ratios lead to type II isotherms, indicative of either non-porous or macroporous materials [52]. When the feed ratio is higher, the curves (gradually) flatten out more at higher relative
- 318 pressures, indicating an absence of further multilayer adsorption. The isotherms are characterized by a closing of the desorption isotherm at  $0.42 \text{ p/p}_0$  while simultaneously lacking a steep sharp capillary
- 320 condensation step. The relative pressure at which the multilayer sorption reaches a second inclination point is the lowest for the sample with the highest Ti/2P and increases as the Ti/2P ratio is
- 322 lowered. This is the clearest for the TiO<sub>2</sub>-C8 materials (Figure 5a) where an inclination point is located at 0.74, 0.85 and 0.93 for the C8-20, C8-5, and C8-3 materials, respectively. The TiO<sub>2</sub>-C8-2 material no
- 324 longer displays an inclination point and represents an H3 hysteresis loop with a type II isotherm. Due to the complex transitional nature of the different isotherms, it is hard to describe the exact pore
- 326 structure accurately. The isotherms however point towards a mesoporous structure resembling

either an aggregation of particles or a stacking of plate-like particles. Additionally, the lower Ti/2P

- 328 materials can contain some smaller-sized macropores. Similar isotherms as for the high Ti/2P ratio hybrids have also been observed for zirconia hybrid materials by Clearfield et al. [21] and titania
- 330 materials by Zhang et al. [53]. In the case of  $TiO_2$ -C3 (Figure 5d), feed ratios above five also lead to the disappearance of the H2(a) hysteresis loop, leading to type I/II isotherms. This shows that these
- 332 materials have lost their mesopore-size structure and are solely microporous in nature, similar to the TiO<sub>2</sub> material synthesized without DPA, and indicating the large effect of DPA incorporation on the
- resulting structures (SI, figure S8). In addition to the isotherm evolution, the diminishment of the pore size with increasing Ti/2P ratio is also supported by DFT (Figure 5b, d) and BJH (SI, Figure S9 and
- 336 Figure S10) modelling. Contrary to the alkyl-based materials, the porosity of the phenyl-based materials is relatively independent of the feed ratios applied, revealing a minor impact of PhDPA
- 338 incorporation on the pore size (Figure 6e, f; SI, Figure S9). This is related to the <sup>31</sup>P-NMR spectra of the PhDPA hybrids, showing the least peak shifts as a function of the feed ratio.
- 340 The BET surface areas (Table 2) confirm the above observations. The phenyl-based materials have a similar  $S_{BET}$  value for different feed ratios, hovering around 300 m<sup>2</sup>/g. This contrasts with the alkyl-
- based materials, where a difference in  $S_{BET}$  in function of Ti/2P feed ratios can be observed. The TiO<sub>2</sub>-C3-3 material reaches the highest  $S_{BET}$  of 379 sm<sup>2</sup>/g, which is lower than found for the recently
- 344 presented hybrid materials from diphosphonate esters showing  $S_{BET}$  values up to 830 m<sup>2</sup>/g [29]. The TiO<sub>2</sub>-C8 materials however display higher surface areas compared to hybrid titania prepared
- 346 nonhydrolytically with diethyloctylphosphonate esters ( $10 240 \text{ m}^2/\text{g}$ ) described in literature [54]. The TiO<sub>2</sub>-C8-1 hybrid has a lower S<sub>BET</sub> compared to its TiO<sub>2</sub>-C3 and TiO<sub>2</sub>-Ph equivalents which might
- 348 be ascribed to the non-porous nature of the unique layered structures observed by NMR and TEM for this hybrid (Figure 2,and 3a). However, the lower  $S_{BET}$  of 285 m<sup>2</sup>/g for TiO<sub>2</sub>-C3-1 compared to the
- 350 other TiO<sub>2</sub>-C3 materials cannot be pinpointed to the same effect since no layered structures are observed for TiO<sub>2</sub>-C3-1 since the propyl chains are expected to be too short for intensive van der
- 352 Waals interactions and resulting self-assembly in layered structures. Above Ti/2P feed ratios of 5, the

surface areas decrease, down to 225  $m^2/g$  for TiO<sub>2</sub>-C3-20, which was expected since the surface

354 becomes more and more comparable to this of unmodified TiO<sub>2</sub> having a low surface area of 120  $m^2/g$ .

#### 4. Separation performance of the hybrids in solid-phase extraction (SPE)

In order to evaluate the performance of the hybrid materials, solid-phase extraction (SPE)

- 358 experiments were performed to separate binary solvent mixtures. For the alkyl-based materials, a 4/1 (v/v) methanol/heptane mixture (17/1 molar ratio) was used, while a 4/1 (v/v)
- 360 methanol/pyridine mixture (8/1 molar ratio) was selected for the phenyl-based materials. The selection of the solvent mixtures was based on miscibility and possibility to benchmark separation
- 362 performance with commercial silica columns (BAKERBOND<sup>™</sup>). The silica (BAKERBOND<sup>™</sup>) have a similar carbon content as TiO<sub>2</sub>-C8-3. The eluate was collected and analyzed with <sup>1</sup>H-NMR in order to
- quantify the residual amounts of heptane and pyridine in the eluates (Figure 6 and SI, figure S11).The separation of the methanol/heptane mixture works well for both the propyl and octyl modified
- 366 samples (Figure 7). These materials display an increased separation performance with an increasing amount of DPA incorporated. For the octyl-modified materials, the residual amounts are 42.5, 44.4,
- and 48.4% for TiO<sub>2</sub>-C8-1, TiO<sub>2</sub>-C8-3, and TiO<sub>2</sub>-C8-5, respectively. Despite the significant increase in C8 functionalities for TiO<sub>2</sub>-C8-1 as compared to TiO<sub>2</sub>-C8-3, only a small difference in residual heptane is
- 370 observed (42.5 versus 44.4%). This can be ascribed to the presence of layered structures for  $TiO_2$ -C8-1 as described above. The organic part is most probably tightly packed in these layered structures,
- 372 limiting the overall accessibility to interact with the heptane molecules and thus reducing the retention capability.
- 374 In comparison to the commercial C8 BAKERBOND<sup>™</sup> SPE Octyl column (70% residual heptane), the TiO<sub>2</sub>-C8 materials show superior separation capability, even when the carbon content is lower as for
- 376  $TiO_2$ -C8-5. The propyl-modified materials display a higher percentage of residual heptane in the eluates, indicating less retention of the heptane. The residual heptane in the eluate is 61.3% for TiO<sub>2</sub>-

- 378 C3-1, and increases to 75.9% for the  $TiO_2$ -C3-5 hybrid with the lowest carbon content. This better performance of the C8-hybrids as compared to the C3-hybrids can be rationalized by the higher
- 380 inherent hydrophobicity of the octyl chains compared to the short propyl chains, leading to an improved separation capability because of more efficient van der Waals interactions between the
- 382 long octyl chain of ODPA and the long heptane chains. Additionally, a slightly different pore structure could also lead to slight variances in sorption behavior. Nevertheless, it should be noted that  $TiO_2$ -C3-
- 384 1 still outperforms the commercial C8-column, probably due to the higher carbon content in combination with the high accessibility of the incorporated organic groups.
- 386 The only  $TiO_2$ -Ph column which shows some pyridine retention (94.7% residual pyridine in the eluate) is this containing the  $TiO_2$ -Ph-1 hybrid material with the highest amount of phenyl groups. The
- commercial phenyl BAKERBOND<sup>™</sup> SPE Phenyl column as well as the TiO<sub>2</sub>-Ph-3 and TiO<sub>2</sub>-Ph-5 columns all show negligible separation behavior with nearly 100% of the pyridine in the eluates. This
- 390 underperformance of the phenyl-modified columns as compared to the alkyl-modified columns can be ascribed to the stronger solvent interactions between methanol and pyridine as compared to
- those between methanol and heptane. As a result, the pyridine co-elutes with the methanol through the column. In general, the SPE experiments, especially those with the  $TiO_2$ -C8 and  $TiO_2$ -C3-1 hybrids,
- demonstrate the accessibility of the organic groups in the hybrid structures and theircompetitiveness with comparable, commercial silica C8-columns. The results clearly reveal the
- 396 potential of these alkyl-modified materials as selective sorbents to treat contaminated waste streams as well as to up-concentrate desired analytes.

398 5. Conclusion

Novel porous titanium organophosphonates based on three different diphosphonic acids and

- 400 Ti(OBu)₄ were synthesized using a hydrothermal, template-free method. Controlled quantitative incorporation of the different phosphonic acids was achieved for various Ti/2P ratios. Higher Ti/2P
- 402 ratios were found to result in more crystalline hybrid structures, closer in characteristics to anatase

TiO<sub>2</sub>, as also indicated by the corresponding surface area characteristics of the hybrid materials,

- 404 demonstrating that the incorporation of the diphosphonic acids has structure-directing capabilities. Structures formed by including a high amount of diphosphonic acids (low Ti/2P), have an enhanced
- 406 porosity, and the anatase crystallization is more hampered due to the higher coverage of the titania with strongly anchored diphosphonic acid spacers, leading to amorphous structures with less-defined
- 408 chemical environments for the phosphonate groups. This is more pronounced for hybrids obtained with alkyl-based diphosphonic acids as compared to hybrids prepared with phenyldiphosphonic acid
- 410 due to the inherent stiffness of the phenyl ring and resulting conformational constraints as demonstrated by simpler <sup>31</sup>P NMR spectra. In addition, a clear and systematic shift in the denticity of
- 412 the phosphonate-titania binding can be observed in the <sup>31</sup>P-NMR spectra, indicating an increased coordination of the phosphonic acid group to the titania surface at higher Ti/2P ratios. Upon
- 414 increasing the feed ratio to Ti/2P = 1 for octyldiphosphonic acid (ODPA), non-porous, layered structures are formed which are easily recognizable in <sup>31</sup>P-NMR spectra by their characteristic upfield
- 416 chemical shift. Regarding solid phase extraction (SPE) efficiency, the phenyl-modified materials showed the lowest solvent separation capability, but their separation capacity for other aromatic
- 418 solvents will be evaluated in future since the lower separation performance for the methanolpyridine mixture might be linked to H-bond interactions between methanol and pyridine. The
- 420 octyldiphosphonic acid derived hybrids (TiO<sub>2</sub>-C8) can remove over 50% of the heptane, compared to the commercial C8 column which removed 30%, showing outstanding performance. Alkyl
- 422 functionalized hybrid titania phosphonates demonstrated potential to up-concentrate desired analytes from waste streams and to tune sorption behavior.

#### 424 Author contribution

Bram Pawlak: Conceptualization, methodology, Validation, Investigation, Writing-original draft,

426 Visualization. **Wouter Marchal**: Conceptualization, methodology, Validation, supervision, Writingreview & editing. **Bharadwaj Mysore Ramesha**: Conceptualization, methodology, Writing-review &

- 428 editing. **Bjorn Joos**, Investigation, Validation, Visualisation, Writing-review & editing. **Lavinia Calvi**: Investigation, Validation, Visualisation, Writing-review & editing. **Jan D'Haen**: Investigation,
- 430 Validation, Visualisation, Writing-review & editing. **Bart Ruttens**: Investigation. **An Hardy**: Writingreview & editing. **Vera Meynen**: Conceptualization, Methodology, Writing-review & editing,
- 432 supervision, Funding acquisition. **Peter Adriaensens**: Conceptualization, Methodology, Writingreview & editing, supervision, Funding acquisition. **Robert Carleer**: Conceptualization, Methodology,
- 434 Writing-review & editing, supervision, Funding acquisition.

# **Declaration of competing interest**

436 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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# 576 Tables

Table 1. ICP-AES results show the Ti/2P ratio for the different titania phosphonate hybrid materials. The error is calculated

Feed ratio Ti/2P	TiO <sub>2</sub> -C3	TiO <sub>2</sub> -C8	TiO₂-Ph
1	$1.31 \pm 0.03$	$1.08 \pm 0.02$	$1.09 \pm 0.01$
2	2.03 ± 0.05	2.12 ± 0.03	1.96 ± 0.03
3	$3.14 \pm 0.04$	$3.13 \pm 0.04$	3.08 ± 0.05
4	4.03 ± 0.06	4.27 ± 0.08	4.19 ± 0.07
5	5.13 ± 0.09	5.18 ± 0.06	5.18 ± 0.08
10	10.68 ± 0.43	9.69 ± 0.21	8.87 ± 0.12
20	23.97 ± 0.96	24.64 ± 0.33	25.36 ± 0.63

578 based on the error propagation of the RSD values on the ICP-AES measurements.

580 Table 2. BET surface areas found by  $N_2$ -sorption for TiO<sub>2</sub>-C3, TiO<sub>2</sub>-C8, and TiO<sub>2</sub>-Ph materials (error <10%).

	BET surface area (m <sup>2</sup> /g)			
Ti/2P	TiO <sub>2</sub> -C3	TiO <sub>2</sub> -C8	TiO <sub>2</sub> -Ph	
1	285	233	310	
2	336	293	334	
3	379	326	309	
5	348	329	319	
10	306	289	299	
20	225	283	279	
TiO <sub>2</sub>	120			

#### 582 Figure Captions

Figure 1. Flow chart of the synthesis procedure.

Figure 2. <sup>31</sup>P CP/MAS NMR spectra of TiO<sub>2</sub>-C8 (a), TiO<sub>2</sub>-C3 (b), and TiO<sub>2</sub>-Ph (c). The 8 ppm signal is clearly visible for the TiO<sub>2</sub>-C8 material with the lowest feed ratio. An overall downfield shift is observed for increasing feed ratios of the alkyl-modified
 materials.

Figure 3. TEM images of the large, layered (a) and small (b) particles in the TiO<sub>2</sub>-C8-1 hybrid. The large particles have a faint
layered structure, which is only observed for the TiO<sub>2</sub>-C8-1 sample. The small particles also display some anatase formation in their diffraction pattern (Figure S6). Structure proposals are shown on the left.

- 590 Figure 4. Background-corrected XRD patterns and normalized Raman spectra of TiO<sub>2</sub>-C8 (a&b), TiO<sub>2</sub>-C3 (c&d), TiO<sub>2</sub>-Ph (e&f). Only a selected number of patterns and Raman spectra are displayed for clarity. A complete overview and additional
- 592 assignments of the unnormalized Raman spectra can be found in the SI, figure S5 and table S2 respectively. Peaks of anatase are clearly visible in both the XRD patterns and Raman spectra for samples with a high feed ratio. Additionally, the XRD
- 594 *patterns evidence some rutile formation.*

Figure 5. N<sub>2</sub> sorption isotherms and DFT pore size distributions for TiO<sub>2</sub>-C8 (a,b), TiO<sub>2</sub>-C3 (c,d),and TiO<sub>2</sub>-Ph (e,f). The curves

- 596 are plotted with an offset on the y-axis to increase the readability (SI, table S3). It should be noted that the kernel used for calculating the DFT PSD's is not perfect and thus only allows a general interpretation of pore size trends. The SI also shows
- 598 the BJH pore size distributions which confirm the trend of larger pores at high feed ratios for the alkyl-modified samples.

Figure 6. Graphical representation of an SPE experiment on a 4/1 (v/v) methanol/heptane mixture (17/1 molar ratio).

- 600 Figure 7. Comparison of the retention capability of hybrid materials obtained with Ti/2P feed ratios of 1, 3 and 5. Alkyl (ODPA and PrDPA) hybrids (left) and phenyl (PhDPA) hybrids (right). The vertical axis shows the percentage of residual
- 602 *heptane (left) or pyridine (right) in the eluate.*

# 604 Figures













