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View Article Online PAPER



Cite this: Mater. Adv., 2025, 6, 1710

Received 24th October 2024, Accepted 27th January 2025

DOI: 10.1039/d4ma01073f

rsc.li/materials-advances

Dynamic imidazolium phosphate@titanium dioxide ionogels as environmental pollutant removers†

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Phosphate-containing ionic liquids display interesting inherent properties including versatile chemical reactivity, thermal and hydrolytic stability and biological response. This contribution focuses on synthesizing diverse imidazolium dialkylphosphates through a simple method involving N-quaternization of 1-alkylimidazole with trialkylphosphate. The use of these building-blocks during sol-gel polymerization of titanium alkoxide affords novel imidazolium phosphate@TiO2 hybrid ionogels. The highest affinity of phosphate towards titanium dioxide results in covalent functionalization of the two phases through stable P-O-Ti bridges, without compromising the molecular dynamic of the embedded ionic liquids. The cationic moiety can be fully exchanged as illustrated using Na⁺ and NH₄⁺ providing access to ionomaterials with adjustable properties. The beneficial effect of the as-prepared dynamic hybrid ionogels was clearly demonstrated by their superior efficiency in removing representative cationic dyes, pharmaceutical pollutants, and metal ions compared to unmodified, native TiO₂.

Introduction

Phosphate-containing ionic liquids stand as a new class of hydrophilic ionic liquids with notable attributes including outstanding reactivity, good thermal stability, enhanced hydrolysis resistance, and low toxicity. 1-5 They find applications in diverse fields such as biomass processing, 6-11 oil desulfurization, 12-14 medical biotechnology, 15,16 azeotropic system separation, 17-20 and organic synthesis as solvents and catalysts. 21-26 Remarkably, phosphate ionic liquids are credited for dissolving recalcitrant microcrystalline cellulose, opening exciting avenues in green and sustainable chemistry processing. 2,27-30

Akin to conventional ionic liquids, their liquid state often impedes their use as advanced solvents and electrolytes, especially in applications requiring solid forms. 31,32 Challenges include high viscosity, low diffusion coefficients, purification and recycling difficulties, and high costs.33

One strategy to address these issues, particularly fluidity, is to immobilize ionic liquids on porous matrices. 34-36 This can be achieved through physical confinement inside of the porous

network or covalent grafting on the surface. 34,35 The final properties can be adjusted for specific applications by modifying either the cationic or the anionic group of the starting ionic liquid as well as the selected porous carrier. 34,35,37,38 Covalent grafting requires ionic liquids bearing specific groups like trimethoxysilyl, dimethylphosphonate, or thiol, along with supports having reactive surfaces, e.g. hydroxyl groups in the case of silica. 34,35,39,40 For inert porous matrices like porous carbon and metal, additional surface pretreatment is required to introduce functional groups like hydroxyls. 41 Covalent attachment prevents ionic liquid migration, and mitigates drawbacks like high viscosity and slow gas diffusion while lowering costs and improving thermal and chemical stability. The fruitful combination of high surface area supports with unique ionic liquid properties lends utility to various domains including catalysis, gas separation, energy storage, lubrication enhancement, and carbon material production. 34,35,37,39,40

While the interaction of ionic liquids and silica hosts has been deeply studied, including either the entrapped or covalently linked forms, 42-50 this was not the case for non-siliceous metal oxide carriers, where few examples were comparatively reported. 51-53 With this aim, we herein report a straightforward synthesis of phosphate-containing ionic liquids (PIL_n) featuring 1,3-dialkylimidazolium paired with various dialkylphosphates. These ionic building blocks were used to develop novel nanostructured hybrid ionogels (PIL_n@TiO₂) through sol-gel processing, involving the co-condensation of the phosphate anion with TiO2. Owing to the highest affinity of phosphate to titanium

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[†] Electronic supplementary information (ESI) available: Apparatus and analytical procedures; experimental details; infrared spectra; supplementary liquid and solid NMR spectra; N2 adsorption/desorption isotherms and textural parameters; supplementary XRD and Raman spectra. See DOI: https://doi.org/10.1039/

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dioxide, the embedded ionic liquids form stable Ti-O-P bonds with the ceramic phase. The dynamic character of these hybrid ionogels was substantiated through spectroscopic analysis and further corroborated through cationic exchange. The imidazolium cation was indeed replaced by Na+ and NH4+ cations, without disrupting the way that anionic phosphate binds to titanium dioxide. We further demonstrate the efficiency of $PIL_n@TiO_2$ for the removal of methylene blue as a representative cationic dve. tetracycline as a representative pharmaceutical antibiotic, and $Fe^{(III)}$ and $Au^{(III)}$ as metal ions from aqueous solutions.

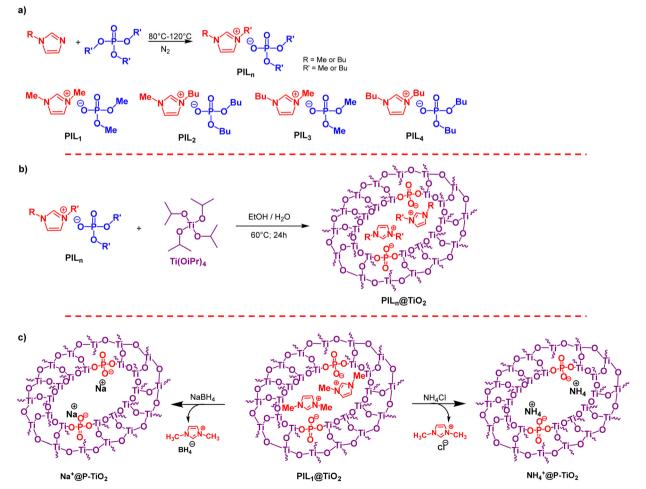
Results and discussion

Synthesis of phosphate ionic liquids (PIL_n)

Phosphate ionic liquids were prepared via direct alkylation, involving the N-quaternization of 1-alkylimidazole with a slight excess of trialkylphosphate (1.2 eq.) under a nitrogen atmosphere (Scheme 1a). ¹H NMR monitoring showed that the quaternization kinetics slowed as the phosphate's alkyl chain length increased. In a 1:1.2 ratio of alkylimidazole to trialkylphosphate, complete conversion was achieved after two days at 80 °C with trimethylphosphate versus three days at 120 °C with tributylphosphate. All ionic liquids were isolated in a quantitative yield of \sim 99% and are liquid at room temperature.

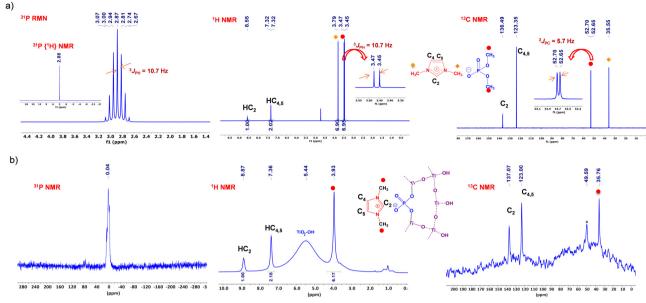
The FTIR spectra of the synthesized phosphate ionic liquids show bands between 2800 and 3000 cm⁻¹ corresponding to the stretching vibrations of alkyl groups (-CH₂- and -CH₃), and bands between 3100 and 3200 cm⁻¹ for the imidazolium ring (-C-H). C=C vibrations appear at 1575 cm⁻¹, while the P=O vibration is observed between 1177 and 1239 cm⁻¹. ⁵⁴ Additionally, a band at $\sim 3400 \text{ cm}^{-1}$ indicates the presence of absorbed water, showing that the hydrophilicity of phosphate ionic liquids decreases with increasing carbon chain length (Fig. S1, ESI†).

Multinuclear NMR spectroscopy confirmed the structure of the synthesized phosphate ionic liquids. The ³¹P NMR spectrum of PIL₁ reveals a complete disappearance of the signal of the starting trimethylphosphate at 3.8 ppm and the appearance in turn of a new septuplet signal at 2.87 ppm (Fig. 1a), due to the coupling of phosphorus with six equivalent protons from the methoxy groups, with a coupling constant of ${}^{3}J_{P-H}$ = 10.7 MHz.⁵⁴ This multiplicity indicates that each phosphate anion is counterbalanced by one imidazolium cation, which consequently excludes the formation of ionic liquids in dimeric



(a) Synthesis of the PILn used in this study, (b) sol-gel method for preparing PIL_n@TiO₂ ionogels and (c) cation exchange carried out on Scheme 1 PILn@TiO2

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(a) Liquid-state (31P, 1H and 13C) NMR of PIL₁ and (b) solid-state (31P, 1H and 13C) MAS NMR of PIL₁@TiO₂

or trimeric states during alkylation. In the ¹H NMR spectrum of PIL₁, the imidazolium proton appears at 8.55 ppm, with symmetric protons at positions 4 and 5 showing a doublet at 7.32 ppm. A doublet at 3.97 ppm corresponds to the six symmetric hydrogens on the two methyl groups at positions 1 and 3, with a weak coupling constant of 0.7 Hz. The dimethylphosphate anion signal was shown at 3.46 ppm, with a coupling constant of ${}^{3}J_{P-H} = 10.7$ Hz that is fully consistent with the ${}^{31}P$ NMR spectrum as discussed above. The ¹³C NMR spectrum of PIL₁ displays peaks at 136.49, 123.35, and 35.55 ppm, corresponding to the carbons C2, C3, and N-CH3, respectively. The signal from the dimethylphosphate carbon appears as a doublet at 52.67 ppm, indicating a coupling constant of ${}^2J_{C-P} = 5.7$ Hz between carbon and phosphorus (Fig. 1a). The chemical structure of the other phosphate ionic liquids was also elucidated by multinuclear (1H, 13C, 31P) NMR spectroscopy and provided in the experimental section (Fig. S2-S4, ESI†).

Preparation of PLI, aTiO2 hybrid ionogels

The synthesis of PIL_n@TiO₂ was achieved through a two-step process involving hydrolysis and condensation of titanium tetraisopropoxide $(Ti(OiPr)_4)$ in the presence of PIL_n (Scheme 1b). Initially, phosphate-containing ionic liquid was dissolved in ethanol, and then Ti(OiPr)₄ was added at a 1:20 molar ratio. After stirring for 15 minutes, water (2/5 the volume of ethanol) was introduced, resulting in a cloudy solution because of the extent of titanium alkoxide hydrolysis and condensation. The gel was subsequently heated at 60 °C for 24 hours. The resulting solid was filtered, washed with ethanol, and dried at 60 °C to yield a white solid powder of PIL_naTiO₂ ionogel.

The structural composition of the resulting materials has been elucidated through infrared spectroscopy (FTIR) and multinuclear solid-state MAS NMR spectroscopy, including ³¹P, ¹H and ¹³C nuclei. The FTIR spectrum of PIL₁@TiO₂ reveals key bands, including Ti-O-Ti bending vibration at 445 cm⁻¹, hydroxyl groups at 3600-2700 cm⁻¹, and OH groups of physiosorbed water at 1638 cm⁻¹. C=C vibration of the imidazolium cation appears at 1575 cm⁻¹, while the P=O frequency of the phosphate group resonates at 1170 cm⁻¹. The broader band at 1105 cm⁻¹ is assignable to P-O-Ti stretching vibration, thereby confirming the covalent anchoring of the phosphate anion to the TiO2 surface.55 Materials with long alkyl chains show weak C-H stretching modes at 2853-2919 cm⁻¹, indicating the retention of PIL's organic motifs within the TiO2 framework (Fig. S5, ESI†).

The solid-state ³¹P MAS NMR spectrum of various PIL_n@-TiO₂ exhibits a well resolved single signal ranging from approximately -0.04 to -1.32 ppm, attributed to the mineral phase bridged by a phosphate anion through the Ti-O-P(O)-O linker (Fig. 1b and Fig. S6, ESI†). This notable shift toward negative values, from 2.87 ppm for PIL_1 to -0.04 ppm for $PIL_1@TiO_2$, can be attributed to the formation of at least one Ti-O-P bond.⁵⁶ The variation in phosphorus chemical shifts observed with different PIL_n is associated with the nature of the countercation. When the positive charge of the cation decreases due to its inductive donor groups (such as butyl), the negative charge of its phosphate counter-anion becomes more significant, leading to enhanced shielding of the phosphorus. This suggests that the sol-gel process induces condensation between the titanium alkoxide and the alkoxy groups of the phosphate component of the ionic liquid, while maintaining the anionic character stabilized by its counter-cation. The cation remains intact, as confirmed by ¹H and ¹³C NMR spectroscopy.

Surprisingly, the solid-state ¹H MAS NMR spectrum of PIL₁@TiO₂ reveals intense and well-defined peaks corresponding to the protons of the 1,3-dimethylimidazolium cation, alongside a broad peak at 5.44 ppm attributed to the Ti-OH hydroxyl protons on the TiO2 surface (Fig. 1b). The signal at

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8.86 ppm corresponds to the proton in position 2 of the imidazole ring, and the peak at 7.35 ppm represents the two hydrogens in positions 4 and 5 due to molecular symmetry. Additionally, the protons of the methyl group attached to nitrogen appear at 3.92 ppm. The integral intensities correlate perfectly with the number of protons present in the cationic part of the PIL1. Therefore, the absence of the methoxy group peak of the phosphate anion indicates their hydrolysis and release during the sol-gel process. ¹H MAS NMR spectra of PIL₂@TiO₂ and PIL₃@TiO₂ show identical peaks corresponding to 1-butyl-3-methylimidazolium with their integration indicating that they exclusively correspond to the protons of the cation (Fig. 1b and Fig. S7, ESI†). This further confirms the removal of butoxy groups from the anion during the sol-gel process. This phenomenon also occurs in PIL4@TiO2, where all the peaks correspond exclusively to the carbon proton of the butylic groups attached to the nitrogen in the ring (Fig. S7, ESI†). The noticeably narrow signals observed for these ionogels

reflect a pronounced dynamicity of the solid framework and

suggest that the ionic character of the network remains domi-

nant in the solid state, despite the significant network reticula-

tion occurring during sol-gel polymerization.⁴²

The solid-state ¹³C MAS NMR of **PIL**₁@**TiO**₂ exhibits characteristic signals of the 1,3-dimethylimidazolium cation, with carbon resonances of N-CH-N, N-CH—CH-N, and N-CH₃ observed at approximately 137, 122, and 35 ppm, respectively (Fig. 1b). The carbon peak from the anionic part of the starting methyl phosphate, expected around 53 ppm, vanishes. Similarly, in the case of ionogels with other **PIL**_n, the presence of cationic components was also noticed (Fig. S8, ESI†). These spectra collectively demonstrate the absence of peaks corresponding to carbons from the anionic part, consolidating its consumption and the creation of new P-O-Ti bonds during mineralization, while preserving the structure of the cation and its ionic interaction with the phosphate anion.

Thermogravimetric analysis was conducted to assess the thermal stability of these hybrid ionogels. Nearly the same weight degradation of 4% could be observed until 200 $^{\circ}$ C for all PIL_n TIO_2 due to the evaporation of water, alcohols, and

physically adsorbed species. Subsequently, a much steeper slope takes place above 230 °C due to the decomposition of 1,3-dialkylimidazolium, with mass loss increasing with the cation's size (Fig. S9, ESI†). Therefore, ionogels with the same cation exhibit similar thermal behavior. Moreover, compared to TiO_2 prepared under similar conditions, the weight loss beyond 230 °C in $\text{PIL}_1 \text{@TiO}_2$ matches the calculated mass of the 1,3-dimethylimidazolium cation, suggesting its complete incorporation inside of the network (Fig. S9, ESI†).

X-ray diffraction (XRD) analysis of PIL_n(a)TiO₂ shows exclusively crystalline peaks of the anatase phase at 25.2, 37.8, 47.8, 53.9, 62.5, 69.2 and 74.8 corresponding respectively to the (101), (004), (200), (105), (213), (116) and (215) planes (Fig. 2a). The average crystallite size estimated from Scherrer's formula is 5 nm. However, the absence of polyphosphate or layered titanate phosphate peaks indicates that phosphorus is well dispersed in the composite and that TiO2 is sufficiently doped with phosphorus. 57-60 Additionally, another peak was observed at 18° for the PIL₄@TiO₂ ionogel, which could be attributed to the packing of imidazolium ring moieties. This peak may indeed result from the large size of the cation, whose long alkyl chains could facilitate the formation of a certain organic periodicity, reminiscent of the one seen in metal-organic frameworks. For the smaller ionic liquid, this peak was observed at 17.9° when the PIL1 content was increased in the PIL₁@TiO₂ to a molar ratio of 1:5 (LIP₁:Ti(OiPr)₄) (Fig. S10, ESI†). Raman spectroscopy confirms the formation of anatase phase in PIL_n TiO_2 , with distinct vibrational modes observed at 144, 396, 509, and 634 cm $^{-1}$ corresponding to E_g , B_{1g} (O-Ti-O bending), A_{1g} (Ti-O stretching), and E_g (Ti-O stretching), respectively (Fig. 2b).61

Nitrogen adsorption–desorption of $PIL_n@TiO_2$ shows an isotherm profile of type IV, with a hysteresis loop typical of mesoporous materials (Fig. S11, ESI†). While a surfactant-free design was chosen here for its simplicity and cost-effectiveness, $PIL_n@TiO_2$ displayed a consistent specific surface area of 200 m² g⁻¹. The specific surface area is slightly higher for hybrid ionogels with asymmetric cationic and larger PILs (Table S1, ESI†).

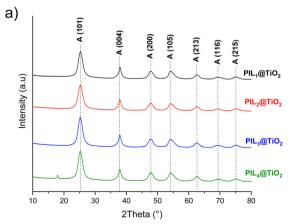
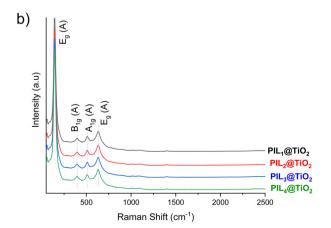


Fig. 2 (a) XRD patterns and (b) Raman spectra of PIL_n@TiO₂.



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Therefore, both the size and volume of the pores increase with the size of the anion, suggesting that the inorganic burst initially nucleates and then condenses with the anionic phosphate near to the surface. It is reasonable to assume the critical role of PIL_n serving as a structure-directing agent and confining medium to grow and crystallize discrete mesoporous anatase nanoparticles. 62,63

X-ray photoelectron spectroscopy (XPS) analysis of PIL₁(a)-TiO₂ reveals the presence of Ti, O, P, N, and C, consistent with the expected chemical composition of the final ionogel (Fig. 3a). The C 1s spectrum can be deconvoluted into three different species, namely C-H, CH₃-N and carbons from the imidazolium ring N-C=C-N and N=C-N components, with binding energies centered at 284.8, 286.3, and 288.6 eV, respectively.⁶⁴ In the nitrogen region, the peak at 401.3 eV corresponds to the nitrogen (N⁺) in the imidazolium cation, while the smaller peak at 398.7 eV is attributed to the nonionized nitrogen in the ring.⁶⁵ These results indicate that the imidazolium cation retains its structural integrity and remains cationic. For oxygen species, the O 1s spectrum displays signals at 529.8 eV and 533.0 eV for oxygen in the oxide lattice (Ti-O-Ti) and on the surface (Ti-OH), respectively.66 The peak at 531.5 eV is associated with P-O-Ti and P=O.67 In the phosphorus region, the P 2p peak can be deconvoluted into two main components located at 133.3 and 134.1 eV assigned to the Ti-O-P bond and phosphate species, respectively. 68,69 The absence of a peak at 133.1 eV corresponding to the P-O-C bond indicates that the two methoxyl groups of PIL1 have been hydrolyzed and condensed with the TiO2 network.⁶⁹ The high-resolution Ti 2p spectrum was deconvoluted into peaks at 458.5 eV (Ti 2p_{3/2}) and 462.2 eV (Ti $2p_{1/2}$), confirming Ti-O bonds in the Ti⁴⁺ state. The negative shift of Ti 2p_{3/2} from the typical 459.3 eV in TiO₂ is attributed to phosphorus doping and oxygen defects.⁷⁰

Scanning electron microscopy (SEM) images of PIL₁@TiO₂ reveal the formation of aggregates of spherical nanoparticles approximately 100 nm in size (Fig. 3b). The uniform size of the primary particles and the absence of large crystals indicate a controlled sol-gel polymerization, corroborating our assumptions

that PIL₁ plays a pivotal role in directing the nucleation and growth of the anatase mineral phase. Energy-dispersive X-ray spectroscopy (EDX) mapping of the elemental composition of both organic and inorganic phases reveals a uniform distribution of phosphorus and titanium throughout the microstructure. This provides convincing evidence for the intimate hybridization of PIL1 and TiO2 within the network, without phase separation or segregation (Fig. 3b).

Cation exchange on PIL₁@TiO₂

PIL₁@TiO₂ was next subjected to cation exchange. This route could provide a route for expanding the molecular diversity of the dynamic ionogels and further tailoring its properties. The exchange was executed using two reagents (NaBH4 and NH4Cl) to replace 1,3-dimethylimidazolium cations in PIL1@TiO2 with Na⁺ and NH₄⁺, resulting, respectively, in the formation of Na⁺@P-TiO₂ and NH₄⁺@P-TiO₂ (Scheme 1c).

The exchange reaction was performed in ethanol, where PIL₁@TiO₂ was dispersed. A stoichiometric amount of the exchanging agent relative to 1,3-dimethylimidazolium was added. After stirring for 4 hours, the mixture was filtered and thoroughly washed with ethanol, and the solid was dried at 60 °C. Cation exchange was monitored by FTIR analysis, focusing on the C=C band of the imidazolium ring at approximately 1573 cm⁻¹. The absence of this signature for NH₄⁺(a)P-TiO₂ indicates complete exchange of the 1,3-dimethylimidazolium. In contrast, for Na⁺@P-TiO₂, the sharp band transformed into a broad band (Fig. S12, ESI†). Solid-state ³¹P MAS NMR spectroscopy of Na⁺@P-TiO₂ and NH₄⁺@P-TiO₂ showed broad signals at $\delta = -0.17$ ppm and $\delta = -1.07$ ppm (Fig. S13, ESI†). These peaks indicate the intactness of the phosphate moiety after the exchange reaction, with the slight chemical shift difference attributed to the nature of the counter-cation. Solid-state 13C MAS NMR confirms the disappearance of the characteristic peaks of the 1,3-dimethylimidazolium cation (Fig. S14, ESI†), demonstrating effective exchange with both sodium Na+ and ammonium NH4+ cations.

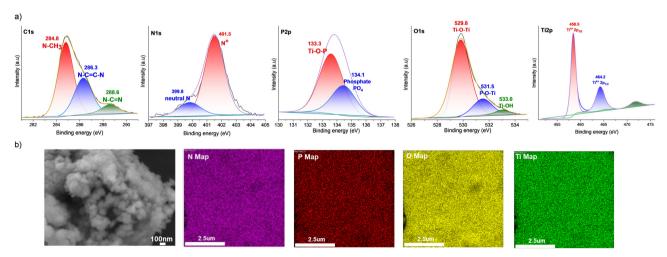


Fig. 3 (a) XPS spectra and (b) SEM image/elemental analysis mapping by SEM-EDX of N, P, O and Ti of PIL1@TiO2

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b) a) 100 100 98 96 95 Weight(%) 94 92 90 90 Na⁺@P-TiO₂ 88 PIL.@TiO. 86 NH₄+@P-TiO₂ PIL₄@TiO₄ 82 1000 Temperature (°C) Temperature(°C)

Fig. 4 TGA analysis of (a) Na⁺@P-TiO₂ and (b) NH₄⁺@P-TiO₂ compared with the starting material PIL_n@TiO₂.

The thermal weight degradation profile of Na⁺(a)P-TiO₂ was compared to that of PIL1@TiO2 (Fig. 4). The significant mass loss observed in the original ionogel above 230 °C was absent in the inorganic material, with the mass difference between the two materials from 500 °C onward corresponding to the 4% mass of the 1,3-dimethylimidazolium cation present before the exchange. Similarly, cation exchange with NH₄Cl shifted the degradation onset from 260 °C in PIL₁@TiO₂ to 410 °C in NH₄⁺@P-TiO₂, demonstrating enhanced thermal stability of the exchanged materials compared to the original ionogels.

Nitrogen adsorption-desorption isotherms of both materials show a hysteresis loop characteristic of open mesoporous structures (Fig. S15, ESI†). Na⁺(a)P-TiO₂ displays a specific surface area of 194 m² g⁻¹ and an average pore size of 5 nm, indicating a slight shrinkage of the network during exchange. NH₄⁺@P-TiO₂ exhibits a specific surface area of 254 m² g⁻¹, which is 56 m² g⁻¹ greater than that of the parent ionogel. After cation exchange,

both materials retain the crystalline anatase phase, as confirmed by XRD spectra with well-resolved peaks and an average crystallite size of about 5 nm (Fig. S16, ESI†). Raman spectroscopy further supports these findings by revealing the characteristic anatase modes consistent with the XRD data (Fig. S17, ESI†).

Removal of organic pollutants and metal ions from water

Ionic liquids display great affinity for chemical and metal pollutants, but are difficult to recover from the medium because of their inherent solubility.⁷¹ To address this issue, supported ionic liquids including ionogels present a scalable alternative. PIL_naTiO₂ materials were consequently tested for the removal of cationic methylene blue (MB) dve and tetracycline antibiotic (TC), and two metal ions namely Fe(III) and Au(III) from aqueous solutions.

Fig. 5 and Fig. S18, and S19 (ESI†) illustrate the removal efficiency (%) and adsorption capacity (mg g⁻¹) of MB, TC,

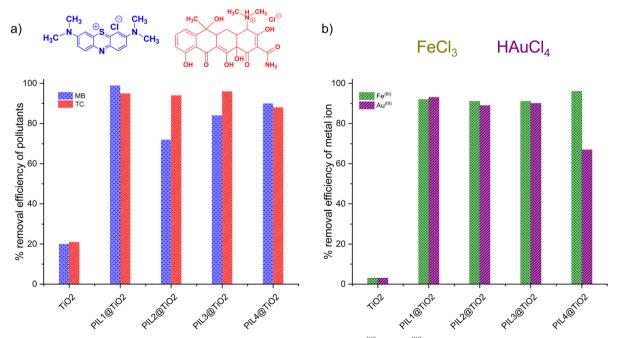


Fig. 5 Removal of (a) methylene blue (MB) and tetracycline (TC), and (b) removal of $Fe^{(III)}$ and $Au^{(III)}$ using FiO_2 and PIL_n are TiO2 materials.

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 $Fe^{(III)}$ and $Au^{(III)}$ using both unmodified TiO_2 and $PIL_n@TiO_2$. Pristine TiO₂ enables only 20% removal of methylene blue, with a low adsorption capacity of 6×10^{-2} mg g⁻¹, contrasting with the enhanced performance reached using PIL_n@TiO₂ (Fig. 5a and Fig. S20, ESI†). The highest removal efficiency (99%) was recorded for PIL₁(a)TiO₂ (99%) and an adsorption capacity of $32 \times 10^{-2} \text{ mg g}^{-1}$.

A similar trend was also observed for the uptake of tetracycline, with unmodified TiO₂ being able to remove only 21%, with an adsorption capacity of 9.33 mg g⁻¹. Comparatively, the removal efficiency attained by PIL_n@TiO₂ exceeds 88%, with adsorption capacities greater than 39 mg g⁻¹. PIL₃@TiO₂ stands as the most effective, with a removal efficiency of 96% and an adsorption capacity of 42.61 mg g^{-1} .

Ionogels also offer substantial potential for metal extraction due to the immobilization of active chemical groups, which leads to a marked increase in the binding capacity of materials for a wide range of metal ions. 72 In our study, unmodified TiO2 demonstrated marginal uptake of 3% for Fe(III) removal, with an adsorption capacity of 0.15 mg g⁻¹. In contrast, regardless of their composition, PIL_naTiO₂ displayed nearly quantitative removal efficiency that exceeds 91%, with PIL4@TiO2 being the best scavenger (96% removal and an adsorption capacity of 4.77 mg g⁻¹). Unmodified TiO₂ was also ineffective for Au^(III) uptake, enabling only 3% removal and an adsorption capacity of 0.85 mg g⁻¹. $PIL_n@TiO_2$ showed spectacular improvements, with PIL₁@TiO₂ achieving the highest removal efficiency (93%) and an adsorption capacity of 25.9 mg g⁻¹. Notably, during the adsorption process, Au^(III) was spontaneously reduced to Au⁽⁰⁾ nanoparticles, as evidenced by the color variation of PIL_n@TiO₂ powders from white to dark purple, 73-75 after filtration and drying of the adsorbents (Fig. S21, ESI†). Overall, these results highlight the interesting performance of PIL_n@TiO₂ compared to unmodified TiO2, with the resulting ionogels being competitive compared to standard absorbents (Table S2, ESI†). Besides, the reducing ability of these ionogels as evidenced for gold, and their high-surface area open new channels of possibilities in the field of heterogeneous (photo)catalysis.

Conclusions

In summary, this study focused on the straightforward preparation of a set of dialkylphosphate-containing ionic liquids, using a catalyst-free, solvent-free, single-step synthesis. Next, the cocondensation of these ionic building-blocks with titanium alkoxide resulted in the formation of novel titanium oxide entrapping imidazolium phosphate ionic liquids. These dynamic hybrid ionogels exhibit several distinctive features, including the formation of stable P-O-Ti covalent bonds, while retaining the ionic character and the mobility of organic moieties as shown by solidstate ¹H and ¹³C NMR of the imidazolium cation, an open porous network formed under surfactant-free conditions, and a crystalline framework built from discrete anatase nanoparticles. The potential for cation exchange within the iono-materials was demonstrated, affecting thermal and structural properties. Additionally, the

hybrid ionogels showed a remarkable ability to remove chemical pollutants and metal ions from water, showcasing their environmental relevance.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by UEMF.

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