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New Nanostructured Zinc Phosphite Templated by Cetyltrimethylammonium Cations: Synthesis, Crystal Structure, Adsorption, and Photoluminescence Properties

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Supporting Information

ABSTRACT: Nanostructured zinc phosphite templated by cetyltrimethylammonium (CTA^+) cations was synthesized using a hydro(solvo)thermal method. This is the first example of a crystalline metal phosphite containing long carbon tails of the CTA^+ ions as templates in its structure, as is structurally characterized by single-crystal X-ray diffraction. The 2D inorganic structures with 4.8^2 topologies are constructed from the interconnection of tetrahedral ZnO_3Br and HPO_3 units, which are sandwiched between CTA^+ ion surfactants in a packing behavior of a largely lamellar liquid-crystalline structure to extend the interlayer *d* spacing to 28.05 Å. Adsorption experiment shows selective adsorption properties of 1-naphthol and a adsorption capacity of 0.17 mmol/mmol (CTA)ZnBr(HPO_3). This compound has potential as an adsorbent for the removal of 1-naphthol pollutant from wastewater. In addition, the naphthol-adsorbed sample shows interesting luminescent properties that are different from that of an as-synthesized sample. The crystal structure, thermal stability, IR spectrum, adsorption, and photoluminescence properties have been studied.

Since the discovery of the Mobil Composition of Matter family of mesoporous silica, the utilization of supramolecular arrays of organic amphiphiles as structure-directing agents in the synthesis of nanostructured materials has been a subject of intensive research.[1] Various kinds of amphiphilic templates and a variety of inorganic precursors give rise to possible combinations that yield a large number of new classes of nanostructured materials. Numerous silica-based materials, metal oxides, chalcogenides, and aluminophosphates with nanoporous structures and large layer spacing have been obtained.[1,2] However, they were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM), and their detailed structural information such as atomic positions and the exact arrangement of inorganic units and surfactant templates is not determined. Previously, Martin et al. reported three crystalline metal halides templated with cetyltrimethylammonium (CTA^+) ion surfactant consisting of largely lamellar liquid-crystalline structures and discrete $ZnCl_4^{2-}$ anions, $Zn_2Cl_6^{2-}$ dimers, and $Cd_4Cl_{12}^{4-}$ tetrameric complex anions, respectively. The metal halide units are all isolated by organic surfactants.[3] To synthesize nanostructured solids and study the correlation between organic amphiphiles and inorganic composition, we now have been interested in the synthesis and structural characterization of surfactant-templated metal phosphates and phosphites by single-crystal XRD. Recently, a series of phosphite materials with 56-, 64-, and 74-membered rings were synthesized by choosing long-carbon-chain monoamines as templates. The carbon-chain skeletons in these compounds were disordered and pointed toward the hydrophobic region of the channel centers.[4] Herein we report the synthesis, structural characterization, adsorption, and photoluminescence properties of nanostructured zinc phosphite, (CTA)ZnBr(HPO_3) (denoted as **1**), in the presence of CTA^+, which not only acts as a structure-directing agent but also forms a largely lamellar liquid-crystalline structure. The atomic positions and orientations of surfactants in **1** are determined by single-crystal XRD.

The hydro(solvo)thermal reactions were carried out in Teflon-lined stainless steel Parr acid digestion bombs at 150 °C for 2 days, followed by slow cooling to room temperature at 3 °C/h. Colorless thin-plate crystals of **1** were obtained by heating a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol), cetyltrimethylammonium bromide (CTAB; 3 mmol), HF(aq) (2 mmol, 48% solution), H_3PO_3 (3 mmol), H_2O (3 mL), and triethylene glycol (7 mL). The bulk product was monophasic, as judged by a comparison of the powder XRD pattern of **1** with a simulated pattern based on the structure analysis results from single-crystal XRD (see Figure S1 in the Supporting Information, SI). The elemental analysis results were consistent with the formula [Anal. Found (calcd): C, 44.77 (44.96); H, 8.36 (8.55); N, 2.74 (2.76)], and energy-dispersive X-ray fluorescence spectroscopy analysis of several plate crystals confirmed the presence of Br, Zn, and P in **1**. The IR spectrum of **1** was recorded by the KBr pellet method. It showed bands characteristic of C−H stretching vibrations of the alkyl chains of the CTA^+ ion at 2917 and 2851 cm^{-1}, P−O groups at 1156 and 1101 cm^{-1}, and P−H stretching vibrations at 2375 and 1037 cm^{-1} (Figure S2 in the SI). Thermogravimetric analysis (TGA) was performed on a powder sample of **1** in flowing air at a heating rate of 10 °C/min between 40 and 900 °C. A huge weight loss of 71.46% was observed in several overlapping steps between 190 and 900 °C (Figure S3 in the SI). The final decomposition product was poorly crystalline based on powder

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XRD. The total observed weight loss of 71.46% was close to the calculated value of 73.40% for the loss of one CTAB molecule and 0.5 H_2O molecules.

Colorless thin-plate crystals of **1** were selected for indexing and intensity data collection on a Bruker X8 Apex2 CCD diffractometer, from which the structure and formula were determined.[5] Compound **1** crystallizes in the centrosymmetric space group $P2_1/c$ (No. 14), and all atoms are in general positions. The asymmetric unit contains one HPO_3 pseudotetrahedron, one ZnO_3Br tetrahedron, and one CTA^+ cation as structural elements (Figure 1a). The Zn atom is 4-fold-coordinated by three phosphite O atoms and one terminal Br atom. The Zn−O bond lengths range from 1.922(3) to 1.942(3) Å, while the Zn−Br bond length is longer at 2.4253(8) Å, resulting in a distorted tetrahedral geometry. The P atom is linked to three Zn atoms through O atoms and leaves one P−H group. The CTA^+ cation contains an ammonium headgroup and a long carbon tail. The ZnO_3Br and HPO_3 tetrahedra are connected to each other to form a 2D network structure with 4.8^2 topology, wherein each 4-ring is enclosed by four 8-rings and each 8-ring is further enclosed by four 4-rings (Figures 1b and S4 in the SI).

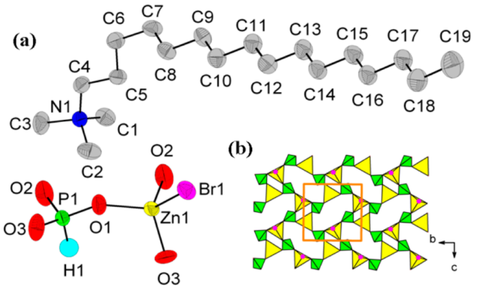

Figure 1. (a) Asymmetric units in the structure of **1** showing the atom-labeling scheme. (b) Section of an inorganic layer with 4.8^2 topology in **1** viewed along the *a* axis. The yellow and green polyhedra represent the ZnO_3Br and HPO_3 tetrahedral units, respectively. The pink, yellow, blue, light-blue, gray, and red circles indicate the Br, Zn, N, H, C, and O atoms, respectively.

As shown in Figure 2, the CTA^+ ion surfactants form largely lamellar liquid-crystalline structures sandwiched by inorganic layers, in which the Zn−Br bonds point to the interlayer space. Compound **1** exhibits an interlayer *d* spacing of 28.05 Å, which is the largest separation observed in crystalline phosphite/phosphate solids because of the packing behavior of single-tailed CTA^+ ions in a bilayer between inorganic 2D networks. The interaction between surfactant molecules and inorganic layers can be inferred from Br···H distances of 3.07−3.83 Å.

The concept of liquid-crystal templation illustrates a process by which the formation of inorganic−organic hybrid materials may be achieved, whereby organic species assemble as a central structure about which inorganic units grow, resulting in a variety of organized nanostructured materials.[6] Many surfactant-templated compounds with large pore sizes and layer gaps have been reported.[1,2] The structures and compositions for these compounds have been characterized by powder XRD, scanning electron microscopy, TEM, and NMR spectroscopy. However, no crystallographic data have been obtained. The study presented herein is the first example of using CTA^+ ions as structure-directing agents in the formation of crystalline zinc phosphite and of determining its crystal structure by single-crystal XRD.

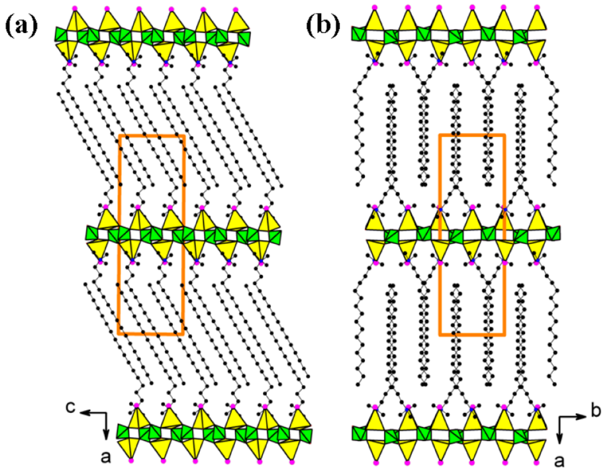

Figure 2. Arrangement of the anionic layers and cationic CTA^+ ion surfactants in the *ac* plane (a) and in the *ab* plane (b). The yellow and green polyhedra represent the ZnO_3Br and HPO_3 tetrahedral units, respectively. The pink, blue, and black circles indicate the Br, N, and C atoms, respectively.

Aromatic pollutants widely exist in wastewater from a variety of industries. These pollutants are easily transported through water into the environment; moreover, they are also harmful to human health. Therefore, the adsorption properties of **1** as an adsorbent for 1-naphthol, pyridine, and phenol were explored. The as-synthesized compound **1** was ground into a fine powder. The adsorbent (0.1 g) was added to 30 mL of a water solution containing the aromatic compounds at room temperature with constant stirring. The solid and solution were separated by centrifugation at 12000 rpm for 30 min in a Kubota 6200 hybrid refrigerated centrifuge. The solution was analyzed for 1-naphthol, pyridine, and phenol using a Hitachi U-2800 spectrophotometer at wavelengths of 212, 257, and 270 nm, respectively. The UV spectra corresponding to the adsorption experiments for pyridine and phenol were unchanged, showing that compound **1** is not an effective adsorbent for these two aromatic compounds. The adsorption amount of 1-naphthol calculated by the relation $Q = V\Delta C/m$,[7] expressed as the molar ratio of adsorbed 1-naphthol to **1**, is plotted as a function of the concentration of 1-naphthol in water. As shown in Figure S5a in the SI, the adsorption processes with 4.5 mM 1-naphthol in water require 3 h to reach equilibrium and compound **1** exhibits reversible adsorption for 1-naphthol molecules. Desorption becomes the dominant process after adsorption reaches the highest value. The adsorption capacity of 1-naphthol on compound **1** is 0.17 mmol/mmol (Figure S5b in the SI). Factors such as the pore size, particle size, and host−guest surface chemistry affect whether the solute is retained on the solid in adsorption processes.[8] The adsorption capacity and mechanism of **1** as an adsorbent for 1-naphthol may be attributed to the particle size and van der Waals stabilization between the 16-carbon tail of CTA^+ and the adsorbate. The remaining solid product after the adsorption experiment was washed with water, separated by centrifugation, and dried, and powder XRD measurements and photoluminescence studies were performed. The XRD pattern for the adsorption experiment with different contact times (1, 3, 7, 9, 13, and 24 h) shows that the sample retains its structural integrity (Figure S6 in the SI). The colors of the as-synthesized and naphthol-adsorbed products were visibly different, changing from white to faint pink. When the samples were irradiated with 254-nm UV light from a hand-held UV lamp, the as-synthesized sample appeared deep purple, whereas the naphthol-adsorbed product emitted blue light (Figure 3).

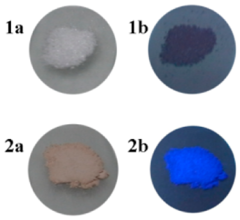

Figure 3. Luminescence properties of **1**: (1a) as-synthesized sample; (2a) 1-naphthol-adsorbed product. The as-synthesized sample emits deep-purple light (1b) and the 1-naphthol-adsorbed product emits blue light (2b) upon exposure to 254-nm UV light.

To study the luminescent properties, the room temperature emission spectra of the as-synthesized sample, CTAB, 1-naphthol, and naphthol-adsorbed product were recorded from 275 to 450 nm using a 254-nm excitation source in a Jasco FP-6300 spectrometer. Similar-structured fluorescence spectra were observed for the as-synthesized sample and CTAB surfactant, indicating that emission of the as-synthesized sample arose from the CTAB molecules. It is interesting that the naphthol-adsorbed product, containing CTAB and 1-naphthol molecules, shows a strong and broad band at about 411 nm, which is different from the emission at 325 nm exhibited by CTAB and at 347 nm exhibited by 1-naphthol (Figure S7 in the SI). Many reports concerning fluorescence of 1-naphthol in an aqueous medium exhibit dual emission peaks for the neutral form at ∼350 nm and the deprotonated form at ∼450 nm.[9] However, a naphthol-adsorbed solid displaying a distinct luminescence from that of its as-synthesized counterpart, CTAB, and neutral and anionic naphthol molecules is observed for the first time. The properties of the emission could be related to $\pi-\pi$ interactions via the orientation and arrangement of 1-naphthol on the surface of **1**.[10] The gas-sorption studies of the title compound for N_2 at 77 K and for CO_2 at 273 K show low surface areas and a limited amount of gas uptake, indicating that the close-packed array of surfactant molecules between 2D inorganic layers does not have voids for gas adsorption.

In summary, the first example of nanostructured zinc phosphite was synthesized in the presence of long-carbon tails of surfactant molecules as templates using a hydro(solvo)thermal method and structurally characterized by single-crystal XRD. Its 2D structure possesses an inorganic sheet with 4.8^2 topology separated by CTA^+ ions with an interlayer d spacing of 28.05 Å. Preliminary adsorption experiments show that compound **1** has potential as an adsorbent for the removal of 1-naphthol pollutant from wastewater. Upon exposure of the naphthol-adsorbed solid to 254-nm UV light, an emission of blue light can be observed. Further research on the control of micelle aggregation to prepare new nanostructured solids with novel functional properties is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data of **1** in CIF format, powder XRD patterns, IR spectra, TGA curves, structural diagrams, adsorption isotherms, powder XRD patterns after adsorption experiments, and luminescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(5) Crystal data for $(CTA)ZnBr(HPO_3)$ (**1**): monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $M_r = 509.79$, $a = 28.080(2)$ Å, $b = 9.3144(6)$ Å, $c = 9.3565(6)$ Å, $\beta = 90.104(2)°$, $V = 2447.2(3)$ Å^3, $D_{calc} = 1.384$ g/cm^3, $\mu = 2.719$ mm^{-1}, 5629 unique reflections with $I > 2\sigma(I)$, R1 = 0.0416, and wR2 = 0.1257. The highest peak and deepest hole were 0.63 and −0.16 e/Å^3, respectively.

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