Luminescent Metal Phosphites

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A Fully Integrated Nanotubular Yellow-Green Phosphor from an Environmentally Friendly Eutectic Solvent**

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Research into the synthesis of nanoporous materials developed from zeolites,[1] aluminosilicates,[2] open-framework metal phosphates,[3–4] coordination polymers,[5] and metal–organic frameworks (MOFs)[6–8] has progressed faster than ever in the last twenty years. MOFs, the most recently established of these materials, have received most attention because of their high hydrogen storage capacity and therefore their potential for use in high-performance fuel cells.[9–10] While major attention has been focused on pore-size-related absorption properties, we have concurrently discovered extraordinary photoluminescence (PL) properties in open-framework metal phosphates.[11–16] We discovered two metal phosphates, NTHU-4[12] and NTHU-6,[13] which have novel nanoporous structures. These metal phosphates, unlike commercialized or developed color-conversion phosphors with emissions that originate from emitting activators doped into condensed host lattices,[17] contained no metal activators or any form of chromophores, but could emit intense yellow light under the excitation of near-ultraviolet (NUV) and blue light. A yellow-light phosphor integrated with a blue light-emitting diode (LED) to produce white light is the current mainstream of display technology,[18] although existing yellow phosphors that can be efficiently excited by NUV or blue light are very limited in number and range. A larger variety of advanced materials to add to the yellow phosphor YAG:Ce (YAG = yttrium aluminum garnet) is therefore in great demand. The intriguing optical properties of NTHU-4 and NTHU-6 has led us to explore a new class of color-conversion phosphors based on nanoporous host structures that have an intrinsic emission mechanism beyond our current understanding.[19]

Existing inorganic yellow-light phosphors are all extrinsic illuminants. Before the two nanoporous structures were reported by us, no inorganic phosphate host that could emit yellow light but was not doped with lanthanide ions had been reported. The extraordinary intrinsic yellow emission was proposed to closely correlate with defects that result from the disorder in the large pores of the structure, firstly observed in NTHU-4 and later in NTHU-6. In the latter study, we had also speculated that the molecule 4,4′-trimethylenedipyridine (tmdp), the common template of both structures, acted as a sensitizer. To affirm and enhance the new phosphor system and rationalize an emission mechanism for the activator-free PL, it was imperative to produce further examples of these structures. In the pursuit of advanced and economical synthetic procedures for making new functional materials, we focused on the environmentally friendly deep eutectic solvent (DES).[20–23] Herein, we report the first nanosized channel structure successfully synthesized in a DES and also the first organically templated gallium oxalatophosphite compound, NTHU-7. It adopts an unprecedented organic–inorganic hybrid nanotubular structure (Figure 1), which exhibits an even more distinctive PL than previously reported phosphates. Five analogues of the NTHU-7 nanotubule and two layer polymorphs, which might be viewed as the two-dimensional unfolded version of the nanotubules, were also prepared in the same DES. Synthesis of these nanotubular materials enabled us to explain the origin of the intriguing yellow luminescence in nanoporous metal phosphates/phosphites (MPOs).

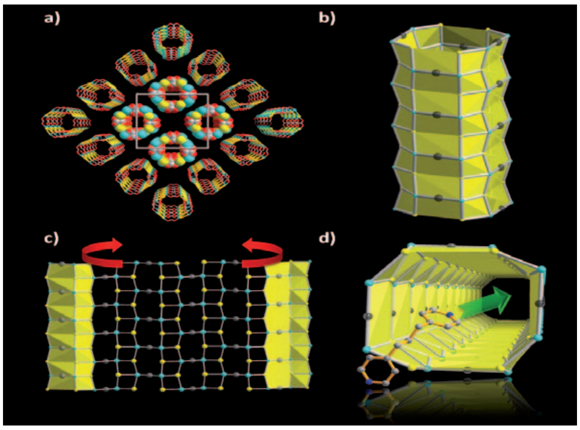

Figure 1. Structure plots of NTHU-7. a) A perspective view of the square-packing nanotubules. Ga centers cyan, P yellow, oxalate groups white and red; b) topological representation of one nanotubule showing the 16R aperture window surrounded by four strips of [$Ga_2(HPO_3)_2$] ribbons and four oxalate groups (gray balls); c) section of the single-layer sheet of the layer polymorph NTHU-7L, which may be viewed as the two-dimensional counterpart of NTHU-7. The red arrows indicate folding to form a nanotubule and d) a NTHU-7 nanotubule with template tmdp. The green arrow indicates that emission can occur as the sensitizer is encapsulated.

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When transparent, colorless solid choline chloride (Ch^+Cl^-, m.p. = 302 °C) was mixed with the white solid oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$, m.p. = 102 °C), liquefaction occurred immediately. With the two organic solids were mixed in a 1:1 molar ratio, miscibility could be achieved completely under ambient conditions to form a water-containing DES.[24] The liquefaction was a rapid endothermic process, with the temperature dropping to as low as 10 °C, which resulted in the formation of a eutectic liquid. Thin crystalline fibers of NTHU-7, which has a unique nanotubular structure, could be synthesized in this DES. The framework of nanotubules is composed of GaO_6 octahedra, bis(bidentate oxalate) ($C_2O_4^{2-}$) groups, and HPO_3 tetrahedra. Single-crystal X-ray structural analysis[25] showed that the chemical composition of the organic–inorganic hybrid nanotubule was $[Ga_2(HPO_3)_2(C_2O_4)(OH)(H_2O)]^-$, where the negative charge was balanced by counterions (Table 1). Each individual nanotubule is constructed from four strips of $[Ga_2(HPO_3)_2]$ four-ring (4R) ribbons connected through four oxalate groups to form a 16-ring (16R) aperture window at the tubule opening (Figure 1 and Figure S5 in the Supporting Information). Lateral eight-ring (8R) windows were also observed to form between adjacent strips of the 4R ribbons. Disordered tetrahedral centers occurred in half of the phosphite groups, which were situated between 16R and 8R windows. The hybrid nanotubule has an external diameter of 16.3 Å and an internal diameter (the measured distance between the closest oxygen atoms across the aperture) of 8.0 Å, which is similar to that of double-walled carbon nanotubes and the inorganic nanotubules of uranyl selenate nanotubules.[26] The NTHU-7 nanotubules are square-packed, with manifold disordered counterions inside and outside each tubule. Based on elemental analysis, thermogravimetric analysis, and solid-state ^{13}C NMR spectroscopy, we confirmed the counterspecies included the Ch^+ ion, the diprotonated tmdp molecule, and lattice water molecules. The reactions seemed to reach high efficiency in atom economy since all components of the DES had participated in the formation of NTHU-7.

Table 1: Chemical compositions of the counterspecies in NTHU-7, five analogues, and two layer polymorphs.

Compound[a]	Counterspecies[b]	Structure type
NTHU-7	$(Ch^+)_{0.5}(H_2tmdp^{2+})_{0.25}(H_2O)_{0.5}$	tubule
tmdpp-NTHU-7	$(Ch^+)_{0.9}(H_2tmdpp^{2+})_{0.05}(H_2O)_{0.5}$	tubule
Cs-NTHU-7	$(Ch^+)_{0.7}(Cs^+)_{0.8}(Cl^-)_{0.5}(H_2O)_{0.5}$	tubule
Rb-NTHU-7	$(Ch^+)_{0.6}(Rb^+)_{0.9}(Cl^-)_{0.5}(H_2O)_{0.5}$	tubule
K-NTHU-7	$(Ch^+)_{0.7}(K^+)_{0.7}(Cl^-)_{0.4}(H_2O)_{0.5}$	tubule
Na-NTHU-7	$(Ch^+)_{0.7}(Na^+)_{0.5}(Cl^-)_{0.2}(H_2O)_{0.5}$	tubule
NTHU-7L	$(Ch^+)_{0.7}(H_2tmdp^{2+})_{0.15}(H_2O)_{0.5}$	layer
Ch-NTHU-7L	$(Ch^+)_{1.0}(H_2O)_{0.5}$	layer

[a] The framework composition was determined to be $[Ga_2(HPO_3)_2(C_2O_4)(OH)(H_2O)]^-$ for all compounds shown in the table. [b] Chloride ions were also found in trace amounts in the compounds prepared in the presence of organic amines, this arises from the energy dispersive X-ray (EDX) analysis technique (Figure S8 in the Supporting Information). The proportions of alkali-metal ions were confirmed by ICP-AES/MS analysis (ICP = inductively coupled plasma, AES = atomic emission spectrometry).

This is the first observation of an organic–inorganic hybrid nanotubular structure in MPOs. The porosity of NTHU-7, estimated in terms of solvent-accessible volume,[27] can be compared to that of the 26-ring (26R) channel phosphite NTHU-5[28] (49.4 % versus 52.1 %), but it can sustain higher temperature (270°C versus 210 °C). As also confirmed by X-ray absorption near-edge structure (XANES) analysis, the nanotubules could be consistently prepared with high reproducibility without oxidation to phosphate ions in the DES medium. The nanotubules could even be obtained by changing the template from 4,4′-trimethylenedipyridine (tmdp) or 4,4′-trimethylenedipiperidine (tmdpp; see the Experimental Section) to alkali-metal ions (such as Cs^+, Rb^+, K^+, and Na^+). Five analogues of NTHU-7 with nanotubular structures, as well as two layer polymorphs (see Table 1) were prepared by using the same water-containing DES. The formation of the tubular structure was presumably DES-driven since the oxalate groups took part in the assembly of the frameworks and choline chloride was included as counterspecies. The water-containing DES thus played an uncommon quintet role as solvent, structure-directing agent, reactant, charge balancer, and space filler. We noted that the specific amount of water within the DES (13.5 wt % from the component $H_2C_2O_4{\cdot}2H_2O$) was critical and created the optimal conditions for the formation of NTHU-7 nanotubules. When anhydrous oxalic acid was used instead of the dihydrate in the DES, no nanotubular phase was obtained.

In theory, tubules may be formed by folding up single-layer sheets, even though the layered counterpart of a nanotubule was difficult to isolate in experiments.[29] Amazingly, a layer polymorph, designated as NTHU-7L, was obtained by introducing HF, a commonly used mineralizer in hydrothermal synthesis, into the reaction for preparing NTHU-7. The prototype layers in NTHU-7L exhibited exactly the same polyhedral connectivity as the nanotubules in NTHU-7 (Figure S4 in the Supporting Information). Each nanotubule can be obtained by folding up a section of the single-layer sheet of NTHU-7L, which contains four $[Ga_2(HPO_3)_2]$ ribbon motifs and four oxalate groups (see Figure 1). It is rather rare to successfully prepare both the nanotubule and its unfolded counterpart and to determine both their structures.

NTHU-7 nanotubules were first observed to luminesce brightly under exposure to long-wavelength UV light (365 nm) from a portable UV lamp. A strong emission with a maximum at 520 nm, regardless of the excitation wavelength of visible light, is shown in Figure 2. The maximum intensity of the emission was detected at $\lambda_{ex} = 460$ nm, with absolute photoluminescence quantum efficiency (PLQE) reaching 46 % and Commission Internationale de l'Eclairage (CIE) coordinates at (0.26, 0.63), which indicates a yellow-green light. When excited solely by UV light, NTHU-7 gave an additional NUV emission centered at 380 nm (CIE coordinates at (0.13, 0.31)), which was dependent on the excitation wavelength. When $\lambda_{ex} = 320$ nm, the yellow-green and NUV emissions reached an equal intensity, which resulted in a green emission with CIE coordinates at (0.24, 0.45). As λ_{ex} entered the visible region, the NUV emission was red-shifted and its intensity decreased, eventually approaching zero. This

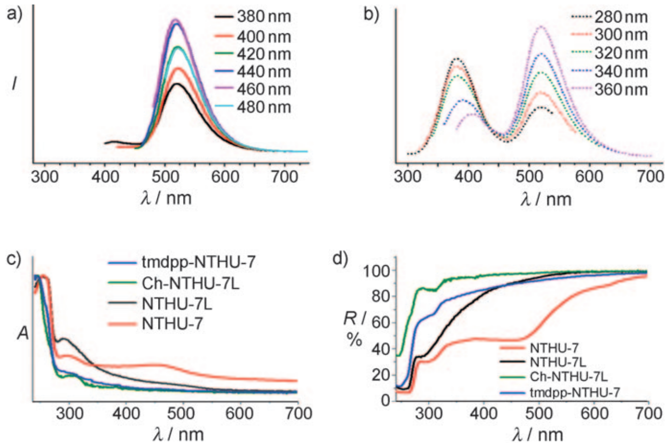

Figure 2. PL and UV/Vis DRS: a) the yellow-green emission at 520 nm with excitation by visible light, b) dual emissions at 380 and 520 nm with excitation by UV light, c) absorption curves, and d) reflectance curves.

result indicated that NTHU-7 nanotubules could be potentially used as a yellow-green phosphor for blue LEDs as well as a green phosphor for UV LEDs.

Currently the color-conversion phosphors that can be excited by UV or blue LEDs are rather limited and are mainly restricted to lanthanide-ion-activated materials. Since no inorganic lattice could emit blue, green, yellow, or red fluorescence without metal activators, the exceptional 520 nm emission from NTHU-7 and the 540 nm and 550 nm emissions from the previously reported NTHU-6 and NTHU-4 are intriguing. The underlying origin of the activator-free luminescence lacked theoretical basis until now. Fortunately, with the discovery of NTHU-7 and its manifold analogues and polymorphs, we could acquire more information for a better understanding of the possible emission mechanism. Firstly, we observed the same structural characteristic of atom disorder as in previous structures on the inner surface of nanotubules in NTHU-7. This observation confirms the correlation of yellow-green emission with the pore disorder in structures as mentioned above. Secondly, we observed no PL for the other compounds listed in Table 1. Because all the nanotubular analogues contained no tmdp template except luminescent NTHU-7, tmdp was confirmed to be involved in the yellow-green emission process. In the UV–visible diffuse reflectance spectra (DRS), we discovered further evidence to establish the role of tmdp. Besides the typical intense absorption peak of the d^{10} (Ga^{3+}) ion in the UV region, only the tmdp-containing NTHU-7 exhibited absorption in the visible region, that is, a low platform-like band extending from 350 nm to about 500 nm (Figure 2 c). However, the presence of tmdp does not guarantee photoluminescence, which was clearly reflected in the nonluminescent NTHU-7L. Further examination of the corresponding reflectance curves (Figure 2 d) showed that the layered NTHU-7L had a higher reflectance ratio than NTHU-7 and thus did not absorb a large amount of light in the visible region. To explain the difference in absorbance, we paid close attention to the host structure and the population of tmdp. The amount of tmdp, although lower in NTHU-7L than NTHU-7, was not an essential factor; however, the location and distance from the host layer should be important. Tmdp, which is situated between the layers, was unlikely to get close enough to the host. However, once the layer became coiled into tubules (Figure 1 d), the distance between encapsulated tmdp and the host would be reduced to allow effective energy transfer, which enabled NTHU-7 nanotubules to luminesce. Based on the above rationale, we further establish the role of tmdp as a sensitizer in the emission mechanism.

The photoluminescence properties of metal phosphites have not been reported to date. The intrinsic PL property of nanoporous MPOs by far can be correlated with the coexistence of three factors: 1) atom-disorder-enhanced defect sites as activators, 2) tmdp template as sensitizer, and 3) a host with nanosized channels. Phosphors that are currently under development for LEDs include four major categories that are based on condensed hosts of metal oxides, metal sulfides, metal nitrides, and alkaline-earth metal oxonitrides. All the phosphors in these categories are extrinsic phosphors with emissions that are activated by dopants through a known fundamental emission process.[18] Now, with the discovery of NTHU-7, we can firmly establish the fifth category: nanoporous MPO-based phosphors. The new phosphors are intrinsic and considered all-inclusive because of the integrity of activator (defect or disorder), sensitizer (tmdp), and host (nanoporous structure) in nature. A near-white LED device (CIE coordinates 0.29, 0.38) was successfully fabricated by coating NTHU-7 nanotubules on top of a GaN blue LED (450 nm; Figure 3 a). Moreover, NTHU-7

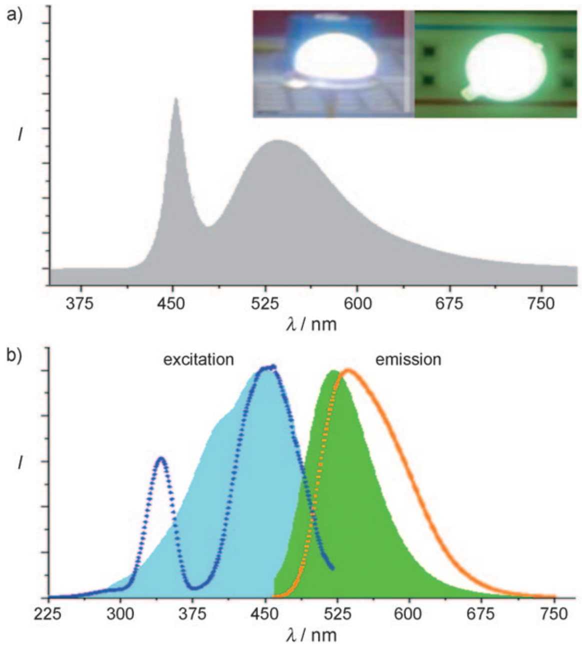

Figure 3. a) Electroluminescence spectrum of a GaN-based NTHU-7 LED. The inset photos show the top and side views of the NTHU-7 coated LED device. b) Relative photoluminescence excitation and emission spectra of NTHU-7 (filled area) and YAG:Ce (dotted curves). NTHU-7 has a wider excitation range than that of YAG:Ce in the NUV region.

could be pumped by a NUV LED (InGaN, 395 nm) chip to make a yellow-green light device (CIE coordinates 0.39, 0.54), whereas YAG:Ce cannot. The wider excitation range of NTHU-7 than YAG:Ce in the NUV region (Figure 3b) constitutes an additional important characteristic of the new phosphor.

We have demonstrated the successful synthesis of the first luminescent metal phosphite NTHU-7, its layered counterpart NTHU-7L, and manifold nanotubular analogues, all with the use of an environmentally friendly organic eutectic solvent. NTHU-7 has a remarkable organic–inorganic hybrid nanotubular structure. Before NTHU-7, nanotubules with complex composition were rarely prepared, and have never been found in MPOs. NTHU-7 is the first activator-free phosphor for UV and blue LEDs. This new class of color-conversion phosphor has a wide excitation range in the NUV and visible region, which is a rare but desirable characteristic that is not present in commercialized phosphors, for example, YAG:Ce. Fabrication of near-white and green LEDs by coating nonlanthanide phosphors on GaN and InGaN chips was first achieved with NTHU-7. We believe this new class of green and yellow phosphors may open a new route to the design of advanced and all-inclusive phosphors for NUV and blue LEDs.

Experimental Section

The nanotubule structure was obtained from a mixture containing 4,4′-trimethylenedipiperidine (tmdpp, 0.4 g, 2 mmol), gallium oxide (0.187 g, 1 mmol), phosphorous acid (0.41 g, 5 mmol), and water-containing deep eutectic solvent of choline chloride/oxalic acid dihydrate (1:1, 5.3 g, 20 mmol), which was heated in a 23 mL teflon-lined autoclave at 160°C for 1 day. The product contained single-phase colorless crystals of tmdpp-NTHU-7 (see below) with a yield of 97% based on Ga. By replacing the tmdpp with 4,4′-trimethylenedipyridine (tmdp, 0.4 g, 2 mmol), the same nanotubular phase of NTHU-7 was obtained (56% yield). The organic amine was substituted in turn with NaOH, KOH, RbOH, and CsOH to successfully prepare four further alkaline analogues, namely Na-NTHU-7, K-NTHU-7, Rb-NTHU-7, and Cs-NTHU-7.

The layer polymorph of NTHU-7 was prepared by introducing HF (0.05 mL, 1.15 mmol) into the reaction mixture for the preparation of NTHU-7. Lamellar crystals of NTHU-7L were obtained as a major-phase product. Another layer polymorph was obtained by introducing the same amount of HF into the reaction mixture for the preparation of tmdpp-NTHU-7. No tmdpp was found in the product, only choline ions. The second layer polymorph was therefore named Ch-NTHU-7L.

CCDC 702980 (tmdpp-NTHU-7), 702981 (Ch-NTHU-7L), 702996 (NTHU-7) and 702997 (NTHU-7L) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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[24] The water-containing DES comprises 13.5% water from $H_2C_2O_4\cdot 2H_2O$ and has a lower melting point ($T_f < 10$°C) than that made from anhydrous oxalic acid, see Ref. [20].

[25] Chemical formula of NTHU-7: $(H_{13}C_5NOH)_{0.5}(H_2C_{13}H_{14}N_2)_{0.25}[Ga_2(HPO_3)_2(C_2O_4)(OH)(H_2O)]\cdot 0.5H_2O$. Crystal data: tetragonal, space group $I4/m$, $M_r = 533.61$, $a = 24.7693(3)$ Å, $c = 6.2647(1)$ Å, $V = 3843.5(2)$ Å^3, $Z = 8$; $R1 = 0.0893$ and $wR2 = 0.2466$. Since the quality of the NTHU-7 crystals was rather poor, the results were not satisfactory. Improved refinements on the nanotubule structure were obtained by using better-quality crystals of tmdpp-NTHU-7, which has the chemical formula $(H_{13}C_5NOH)_{0.9}(H_2C_{13}H_{24}N_2)_{0.05}[Ga_2(HPO_3)_2(C_2O_4)(OH)(H_2O)]\cdot 0.5H_2O$. The crystal data were the same as NTHU-7 except $M_r = 535.73$, $a = 24.7980(4)$ Å, $c = 6.2683(2)$ Å, $V = 3854.6(3)$ Å^3, $Z = 8$; $R1 = 0.0460$ and $wR2 = 0.1274$. The "squeeze" model was utilized to take account of the contribution of disordered counter species into refinements.

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