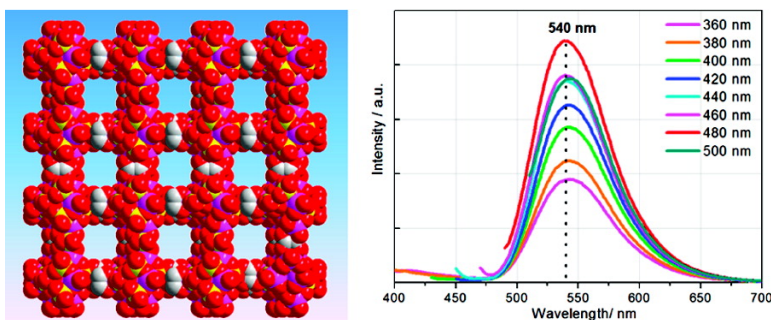


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Intrinsic Yellow Light Phosphor: An Organic–Inorganic Hybrid Gallium Oxalatophosphate with Hexameric Octahedral $\text{Ga}_6(\text{OH})_4\text{O}_{26}$ Cluster

Ya-Ching Yang and Sue-Lein Wang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

Received November 8, 2007; E-mail: slwang@mx.nthu.edu.tw

For the past two decades, microporous metal phosphates have been known for copious structural chemistry¹ with diverse compositions and wide application in conventional industry, such as redox catalysts and molecular sieves, and in modern technology, such as MRI contrast reagents, low- k and hydrogen storage materials.² In recent years, photoluminescence has been discovered to be an interesting new property of microporous materials. For example, some extra large channel zinc and gallium phosphates can emit blue light³ or can even synchronize dual wavelengths (blue and yellow) to give out white light under the excitation of UV light.⁴ This intriguing optical property has allowed us to discover microporous metal phosphates of a new class of inorganic phosphors with distinct emission centers different from conventional understanding.⁵

Yellow light phosphor integrated with blue LED to produce white light is the mainstream of current lighting technology.⁶ Current inorganic yellow light phosphors are yet very limited in number and kind. The quest for more variety of advanced materials in addition to the yellow phosphor YAG has been in great demand. Existing inorganic yellow phosphors are all extrinsic illuminants (i.e., a condensed host lattice with doped lighting elements, e.g., YAG:Ce³⁺,⁶ (Sr,Ca)₅(PO₄)₃Cl:Eu²⁺,⁷ Ba₂Mg(PO₄)₂:Eu²⁺,⁸ Sr₃SiO₅:Eu²⁺,⁹ and α -SiAlON:Eu²⁺).¹⁰ Before the microporous zinc gallophosphate, NTHU-4, no inorganic phosphate host without doped metal activators could emit yellow light. The extraordinary intrinsic yellow emission of NTHU-4 is speculated to closely correlate with defects resulting from the disorderliness near large pores. To establish such a new phosphor system and to be able to verify the distinct origin of emission, it should be invaluable to find further instances. Herein, we report the synthesis, structure, and photoluminescence of a new intrinsic yellow phosphor, NTHU-6, which has a unique MOF-like organic–inorganic hybrid open framework with high PL quantum efficiency (PLQE). It is the foremost hybrid microporous yellow light phosphor and the discovery of its structure that enabled us to further pin down the origin to the remarkable luminescence encountered in the microporous MPO system.

Fiber-like yellow transparent crystals of NTHU-6 were obtained by heating a mixture of 4,4'-trimethylenedipyridine (tmdp), Ga₂O₃, oxalic acid, H₃PO₄, and H₂O with the molar ratio of 4.6:0.5:1.2:5:666 under a mild hydrothermal condition at 180 °C for 48 h.¹¹ The crystals were extremely slender ($\sim 1 \mu\text{m}$ under the examination of SEM, Figure S1), and they grew into bundles from which no single crystals but laminar twins could be isolated. After countless selections, a crystal with the least twinning was carefully scrutinized for single-crystal X-ray diffraction. From the combined results of crystal structure analysis,¹² TGA, EA, ICP-AES, ¹³C, ³¹P, and ⁷¹Ga NMR,¹³ the chemical formula of the crystals was determined to be (H₂tmdp)₂[(Ga₁₀(OH)₄(C₂O₄)₂(HPO₄)(PO₄)₈)] $\cdot 3\text{H}_2\text{O}$.

The framework is composed of five independent Ga sites: Ga(1), Ga(2), and Ga(3) in octahedral and Ga(4) and Ga(5) in tetrahedral centers; six P sites: P(1)–P(5) for PO₄ and P(6) for

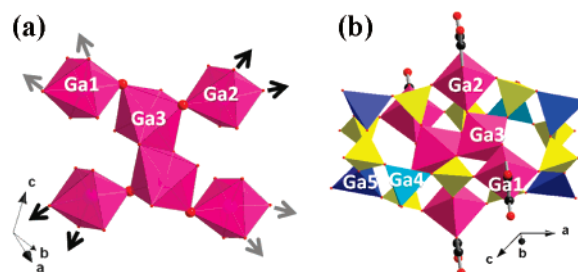


Figure 1. Cluster units in NTHU-6: (a) the hexameric octahedral $\text{Ga}_6(\text{OH})_4\text{O}_{26}$ cluster with bridging OH in red balls. Direction of the arrows indicates four different hexamers connected on the bc plane; (b) the 22-polyhedral SBU with ox groups shown in ball-and-stick model. Yellow tetrahedra are phosphate groups.

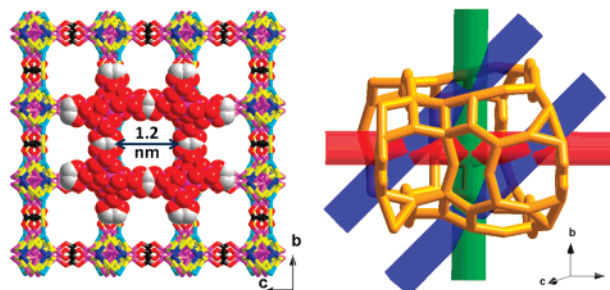


Figure 2. The 3D framework of NTHU-6: (left) wire drawing plus space-filling model to show nanosized channels along [100]; (right) a view of the structure (in brown wire) to show 3D channels along [100], [010], and [110], which are, respectively, highlighted by rods in red, green, and blue.

HPO₄; two C sites for oxalate (ox) and 25 O sites for hydroxyl, phosphate, and ox groups. One of the most striking structural features is in that two $\text{Ga}(\text{OH})_2\text{O}_4$ and four $\text{Ga}(\text{OH})\text{O}_5$ are connected into the unprecedented isolated hexameric octahedral cluster of $\text{Ga}_6(\text{OH})_4\text{O}_{26}$ (Figure 1).

The $\text{Ga}_6(\text{OH})_4\text{O}_{26}$ clusters are interlinked into microporous octahedral–ox hybrid sheets parallel to the bc plane through bis-bidentate ox groups (Figure S2). Each hexamer is also connected to 16 tetrahedra (6 GaO_4 and 10 PO_4) into a 22-hetero-polyhedral secondary building unit (SBU, Figure 1b). The SBUs are connected via Ga–O–P bonds to give 2D inorganic nets running parallel to the ab plane, and they are further linked via the ox linkers along c to give a 3D hybrid framework with three-dimensional nanosized channels (Figure 2). The channels along a - and b -axes are intersecting while they respectively intersect with two sets of [110] channels at a different location. The spacious interior nonframework space was estimated to be up to 53.4% of the unit cell, exceeding all 24 R-channel structures of metal phosphates (Table S1).

The anionic hybrid framework of NTHU-6 is charge balanced by diprotonated tmdp molecules ($\text{H}_2\text{tmdp}^{2+}$) which, together with lattice water molecules, are disordered in the large channel space. Their presence was confirmed by TGA, ¹³C MAS NMR, and EA

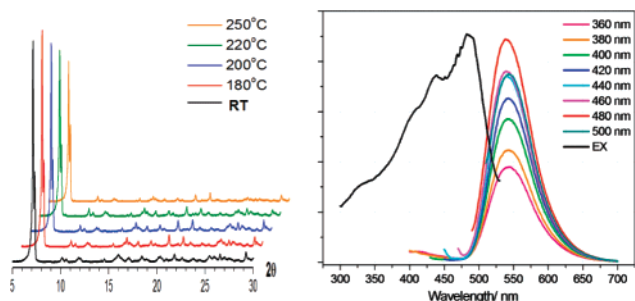


Figure 3. PXRD patterns measured at different temperatures (left) and excitation and emission spectra of NTHU-6 (right).

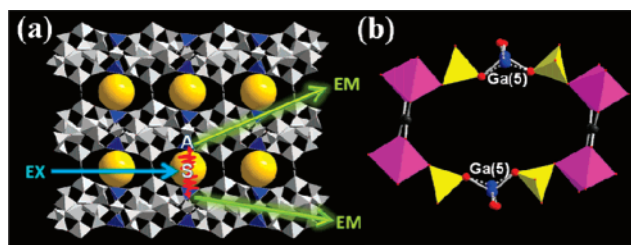


Figure 4. The structure of NTHU-6 with (a) proposed energy transfer path between the sensitizer (S) and activator (A) and (b) a closer look at the disordered Ga sites. The yellow balls in (a) represent the location of $\text{H}_2\text{-tmp}^{2+}$ cations which are in close distance to the activator sites of disordered Ga(5) (in navy tetrahedra).

data. The encapsulated tmp molecule could be retrieved from the crystals of NTHU-6 and further confirmed by ^1H NMR (Figure S5). The results from combined TG/PXRD on heat-treatment samples revealed that the structure of NTHU-6 could be sustained up to 250 °C (Figure 3) and became amorphous over 280 °C.

Due to predominant gathering of the 22-polyhedral SBUs on *ab* planes, the (001) reflection of NTHU-6 shows an overwhelming intensity in both calculated and observed PXRD patterns (Figure S6). Such a preferred orientation inherent in structure is rather rare among 3D framework structures. Furthermore, NTHU-6 could be excited efficiently over a broad spectral range from 360 to 500 nm to emit yellow luminescence invariably at 540 nm, and its absolute PLQE measured using an integrating sphere was up to 42%,¹⁴ about 1.4 times that of NTHU-4. On the basis of the emission spectra, its CIE chromaticity coordinates were calculated at $x = 0.34$ and $y = 0.63$ (Figure S7).

NTHU-6 is an unprecedented intrinsic yellow luminant phosphor with an organic–inorganic hybrid framework. On the basis of previous reports,³ activator-free luminescent MPOs showed a common feature in nanosized channels and typical blue emission due to lattice defects, but the origin of yellow emission is more than that. We had attributed the yellow emission of NTHU-4 to the defect sites from disorderliness in the host lattice. Now, in NTHU-6, we once again discovered two similar disordered sites of Ga(5) (apart by 0.48 Å) near extra large pores (Figure 4). The inference on correlation between structural disorderliness and yellow emission can then be established. Moreover, besides the blue fluorescent NTHU-2,^{3b} yellow-to-white light emitting NTHU-4, and currently the yellow fluorescent NTHU-6, none of the tmp-containing materials were reported to be illuminants. The occluded organic species are thus not considered as activator. In this study, we discovered that the template could absorb 350 nm UV light and dimly emit at 400 nm. In addition, they reside within channels of which Ga(5) is disordered. Therefore, we presumed that the

template might act as a sensitizer^{5b} in assisting energy absorption and transfer as depicted in Figure 4.

This study has demonstrated an unprecedented hybrid yellow phosphor, NTHU-6, which reinforces the scope and depth of microporous metal phosphate as a completely new class of inorganic phosphors. It is remarkable to further discover structural disorderliness from which the origin of intrinsic yellow emission in the extra large channel structure can somewhat be elucidated. Such a subtle structural variation correlated phenomenon would otherwise be impossible to detect and understand without detailed single-crystal structure. Unlike the strategy of using large organic linkers and relatively small metal clusters in the assembly of MOFs,¹⁵ we for the first time prepared a hybrid open-framework structure with nanosized channels by assembling small organic oxalate linkers and large inorganic hexameric octahedral Ga–O clusters. NTHU-6 has higher PLQE than NTHU-4. Besides the typical intense broad absorption band of the d^{10} ion in the UV region, NTHU-6 exhibits a surprising hillock-like absorption band extended into the visible region (Figure S8), which is rarely observed for Ga^{3+} -containing compounds. Further investigation on the optical and possible semiconducting property on microporous metal phosphates will proceed.

Acknowledgment. We are grateful to National Science Council (NSC-96-2628-M007-015) for financial support.

Supporting Information Available: SEM photograph, structure plots, ICP-AES, EA, TGA, NMR, UV–vis spectra, and crystallographic CIF file are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) The product contained two phases: crystals of NTHU-6 (yield ~35%, based on the limiting reagent of Ga) and powders of $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$.
- (12) Crystal data for $[\text{H}_2\text{C}_6\text{H}_4\text{N}_2]_2[\text{Ga}_{10}(\text{OH})_4(\text{C}_2\text{O}_4)_2(\text{HPO}_4)(\text{PO}_4)_8] \cdot 3\text{H}_2\text{O}$: monoclinic, space group $C2/m$, $M_r = 2251.61$, $a = 23.048(3)$ Å, $b = 24.649(3)$ Å, $c = 17.081(3)$ Å, $\beta = 132.192(4)^\circ$, $V = 7189.77$ Å³, $Z = 4$; $R1 = 0.0787$ and $wR2 = 0.2096$. The crystal contained two twin components, and the refinements showed they were about 50% for each.
- (13) See Supporting Information.
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