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Luminescent Materials

Variant Luminescence from an Organic–Inorganic Hybrid Structure with an Isolated 4-Ring Zinc Phosphate Tecton**

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In recent years, the science of materials synthesis has made significant progress with the help of improved preparation methods and advanced characterization techniques. A tremendous number of new crystalline solids have been discovered with novel framework topology, complex stoichiometry, or interesting properties, thereupon leading to innovative applications.[1–7] As the physical properties depend on structure and chemical composition, there is the possibility to produce materials with tailor-made properties by structural modification or tuning of the chemical constituents.[8–11] Examples of the latter case are represented by one of the core technologies in modern LED phosphors, in which different-colored emissions are switched on by doping with various lanthanide ions. As a rule of thumb, any observable changes in physical properties are attributed to variations in the structure or the elemental composition of the material. No examples have ever been demonstrated in which distinct properties were displayed by crystalline phases with identical structures and chemical compositions.

Herein we report an exceptional system of metal phosphates that incorporate organic aryl carboxylates (organometallophosphates, OMPOs), NTHU-10: (Hbpy)[Zn(H_2PO_4)(btec)$_{0.5}$] (bpy = 4,4′-bipyridine, btec = benzene-1,2,4,5-tetracarboxylate, NTHU = National Tsing Hua University), which was observed to violate our common wisdom of structure–property relationships. Four hydrothermal reactions, keeping exactly constant the composition of the initial reaction mixture, were conducted at different temperatures (120, 160, 180, and 200 °C), from which four batches of products were obtained, designated as **10a**, **10b**, **10c**, and **10d**, respectively. As shown in Figure 1, they looked alike as powders or sizable crystals on visual inspection, but they could be differentiated upon exposure to 365 nm UV light. Crystals of **10a** were barely emissive in the blue-light region, whereas **10d** were strongly emissive in green-light region with a significant quantum yield (see below). Judging from the difference in synthesis temperatures (from 120 to 200 °C) and the distinct photoluminescence (PL) from faint blue to bright green for **10a** to **10d**, we assumed that their structures or chemical compositions, or both, would be somewhat different.

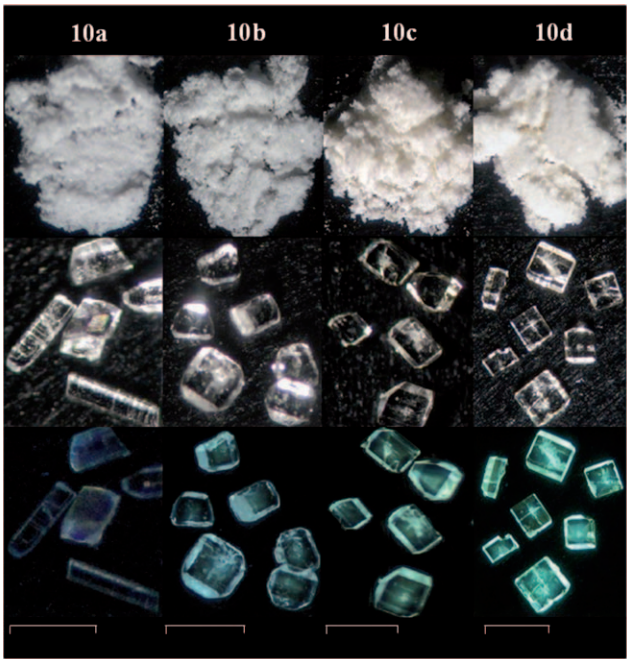

Figure 1. Photos of the four PL analogues in the NTHU-10 system. Top powder, middle single crystals, bottom single crystals under UV light ($\lambda = 365$ nm). Scale bars are 500 μm.

However, the four batches of crystals showed no discrepancy in structure or in chemical composition, as corroborated by elemental analysis (EA) and thermogravimetric analysis (TGA) and by energy-dispersive X-ray (EDX), IR, Raman, and solid-state NMR spectroscopy. Samples **10a** to **10d** are four amazing optical analogues of NTHU-10, which is also the first organometallophosphate structure constructed from zero-dimensional (0D) inorganic building unit (Figure 2). Few 0D inorganic tectons have been observed in metal phosphates.[12,13] It is not straightforward to trim the MPO lattice down to 0D. However, by manipulating the solvent factor in the reaction system of NTHU-8,[14] we were able to control the formation of 1D or 0D inorganic substructures. Discovery of NTHU-10 marks completion of a hybrid framework system that contains all three possible dimensionalities of inorganic tectons (Figure 3).[14,15]

The four optical analogues **10a**, **10b**, **10c** and **10d** were found to share the common structure of NTHU-10.[16] The unique structure contains discrete 4-ring clusters of [$Zn_2(H_2PO_4)_2$]$^{2+}$ as the 0D inorganic substructure, which are interlinked by four-connected btec^{4-} ligands into a hybrid [$Zn_2(H_2PO_4)_2$(btec)]$^{2-}$ layer. Monoprotonated bpy molecules (Hbpy$^+$) were located in the interlayer space, and played a

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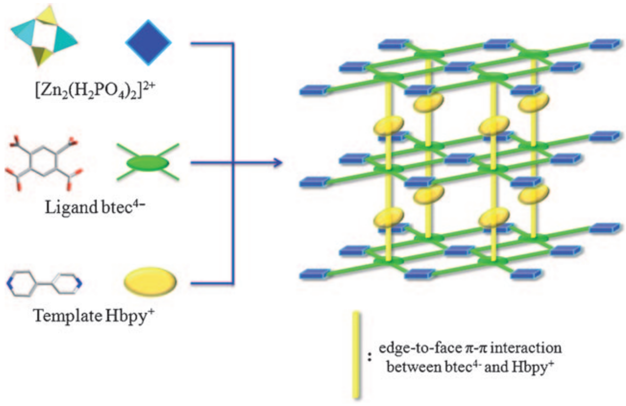

Figure 2. Simplified representation of NTHU-10 showing how the network topology is built from 0D $[Zn_2(H_2PO_4)_2]^{2+}$ clusters connected by btec^{4-} ligand and Hbpy$^+$ template.

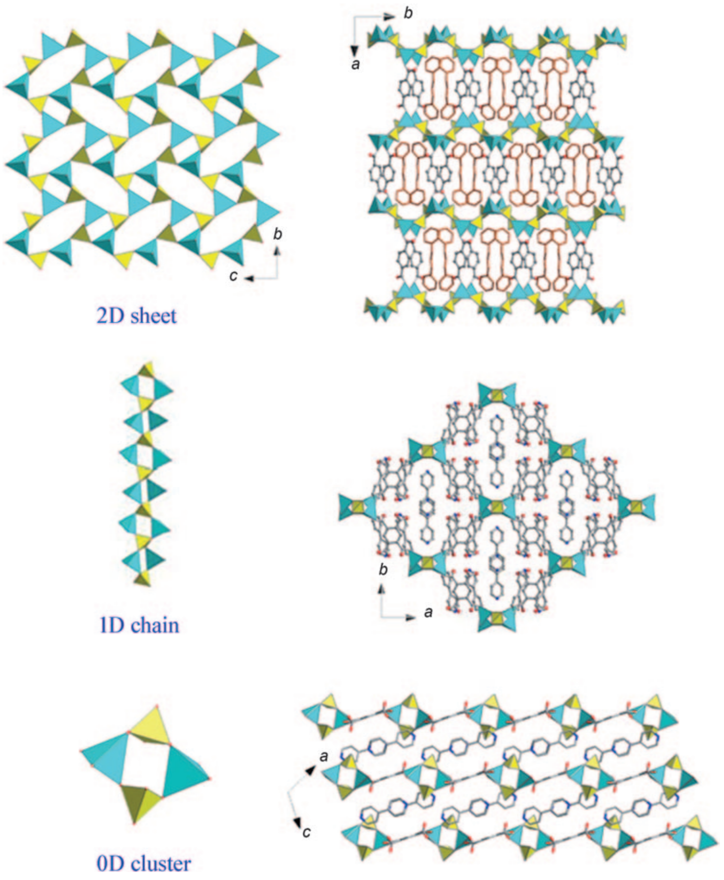

Figure 3. Various inorganic sublattices with progressively decreasing dimensions in OMPO compounds: 2D sheets in NTHU-2,[15] 1D chains in NTHU-8,[14] and 0D clusters in NTHU-10.

dual role of template and charge balancer. Face-to-face π–π interactions (3.47 and 3.86 Å) were observed between adjacent Hbpy$^+$ moieties, which form infinite supramolecular chains running along the *b* axis. Edge-to-face π–π interactions (3.61 Å) were also observed between Hbpy$^+$ templates and btec^{4-} ligands. Therefore, another set of infinite supramolecular chains containing alternating btec^{4-} ligands and $(Hbpy^+)_2$ pairs forms, propagating along the same direction as the hybrid $[Zn_2(H_2PO_4)_2(btec)]^{2-}$ layers. Therefore, such π–π-driven chains impart a supramolecular connected 3D network to the 2D covalent structure and fortify linkages among the organic and the inorganic building units (Figure 2). Besides π–π forces, strong hydrogen bonds are also observed between the organic ligand and the template ($O_{btec}\cdots HN_{bpy}$ 2.75 Å) and between the inorganic 4R units and the template ($O_PH\cdots N_{bpy}$ 2.61 Å). With such a profound number of secondary forces at work in the structure of NTHU-10, it can be expected that various possible energy-transfer pathways exist to provide for luminescence.

All four optical analogues of NTHU-10 were carefully investigated by PL and UV/Vis spectroscopic measurements.[17] As shown in Figure 4a, **10a** displayed a weak emission band centered at 485 nm with faint blue color (Commission Internationale de l'Eclairage (CIE) color coordinates: 0.27; 0.37), whereas **10d** displayed a much stronger emission band composed of three peaks centered at 485, 515, and 550 nm, resulting in bright green light (CIE color coordinates: 0.33; 0.49). It is worth noting that the quantum yield of **10d** was measured to be 11% (based on 90% for YAG reference), superior to most luminescent hybrid materials of MOFs.[4] UV/Vis spectra (Figure 4b) revealed that **10a** could hardly absorb in the visible-light region, which is self-evident for the weak emission. In contrast, **10b**, **10c**, and **10d** showed a common platformlike absorption band extending from 350 to 450 nm, accordingly endowing them with the capacity for more intense emission. Since they all adopt the same structure, the marked difference in PL properties from **10a** to **10d** was suspected to be associated with subtle structural discrepancies, such as the inconformity in atomic disorder between the yellow and white analogues of NTHU-4.[18] We then particularly looked for high-quality crystals of **10a** and **10d** to perform low-temperature diffraction measurements. These two were expected to show the largest deviation in structure or composition, if there was any.

To our surprise, no significant differences in the covalent bonds or supramolecular interactions of **10a** and **10d** were detected (Table S1 in the Supporting Information). At this stage, we tried to identify the specific structural units in NTHU-10 that corresponded to the individual emission peaks in the PL spectra. The blue emission, with a maximum at 485 nm in **10a** to **10d**, was conjectured to emit from the inorganic $[Zn_2(H_2PO_4)_2]^{2+}$ part of NTHU-10. As noted, certain d^{10} metal phosphates emit in the blue region under UV excitation.[19] For further evidence, a sample of **10d** was heated to decomposition at 400 °C. The residue, confirmed to contain only the inorganic material from NTHU-10, also gave a weak blue emission line at 470 nm (Figure S2a in the Supporting Information), a blue shift by 15 nm as compared with that of **10d**. The result indicated that the emission peak observed at 485 nm for NTHU-10 should originate from the inorganic $[Zn_2(H_2PO_4)_2]^{2+}$ unit. Next, the emission peak at 515 nm was

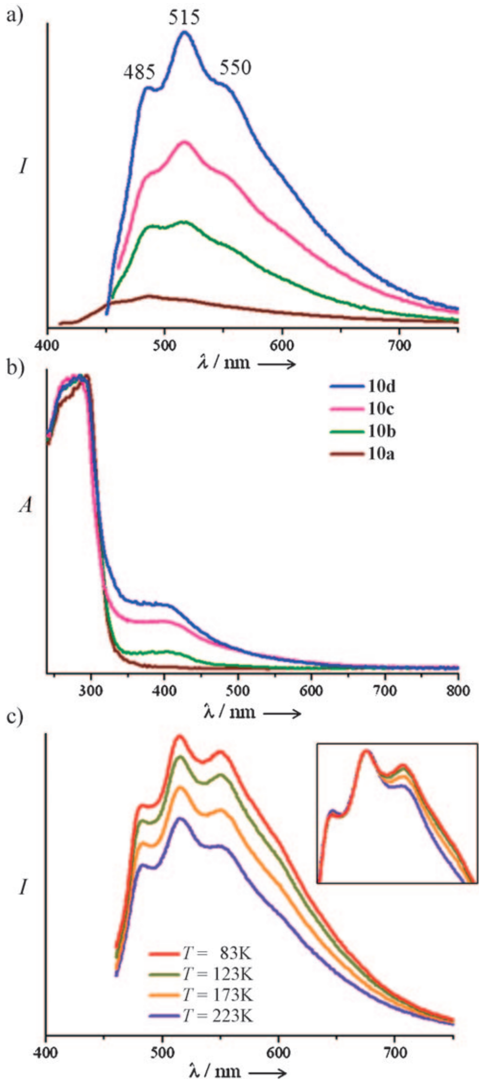

Figure 4. Optical spectra of NTHU-10: a) PL emission spectra after 440 nm excitation and b) UV/Vis absorption spectra measured at room temperature; c) in situ PL emission spectra of **10d** at different temperatures (the inset shows the normalized spectra).

considered to be attributed to ligand-to-metal charge transfer LMCT from O_{btec}–Zn bonds which, as in MOF structures, are often observed in the region from 500 to 530 nm.[4,20] Meanwhile, we prepared a solid sample of K_4(btec)[21] to measure the ligand-based emission of $btec^{4-}$. It occurred at 435 nm, supporting the assignment of the emission peak at 515 nm (a red shift by 80 nm arising from bonding to the Zn^{2+} ion) to LMCT for NTHU-10.

Besides the magnitude of the emission intensities, it was apparent that the occurrence of the yellow emission peak at 550 nm marked a PL property that differentiated **10a** from **10d** (**10b** and **10c** also show this emission). To look into the origin of this emission, we performed in situ PL measurements on **10d**. As shown in Figure 4c, the emission intensities were raised by decreasing the temperature, as most thermal motions and nonradiative relaxations in structure were relieved at lower temperatures. Upon further investigation into the normalized spectra (Figure 4c, inset), we discovered that the extent of intensity change with respect to temperature change was the same for both blue (485 nm) and green (515 nm) emissions, but the enhancement in intensity with decreasing temperatures was much greater for the yellow emission at 550 nm. The result implied the yellow emission to be associated with the more labile components in NTHU-10, that is, $Hbpy^+$ templates, between which, as mentioned above, abundant π–π interactions exist. Similarly, we prepared a solid compound containing protonated bpy cations, $[H_2bpy]Cl_2$, and performed PL measurements. The solid sample of $[H_2bpy]Cl_2$, in which H_2bpy^{2+} moieties are well-packed with significant π–π interactions, gave an emission at 570 nm. But an aqueous solution of $[H_2bpy]Cl_2$ gave an emission at 528 nm (Figure S2c in the Supporting Information).[22] Accordingly, these data supported the conclusion that π–π interactions of $Hbpy^+$ account for the yellow emission at 550 nm from NTHU-10, in which the degree of π overlap of $Hbpy^+$ cations was considered to be in between that of the solid and aqueous forms of $[H_2bpy]Cl_2$.

The complex PL spectra of **10b**, **10c**, and **10d** were elucidated with three emission origins: 1) ZnPO host lattice giving rise to the first peak centered at 485 nm, 2) Zn–O_{btec} bonding, in which charge transfer from the $btec^{4-}$ ligand to the Zn^{2+} center creates the second emission peak centered at 515 nm, and 3) π–π interactions among $Hbpy^+$ cations that generate exciplex emission corresponding to the third peak centered at 550 nm (Figure S3 in the Supporting Information). It is noteworthy that, although the observed π–π interaction distances (Table S1 in the Supporting Information) are exactly the same for **10a** and **10d**, energy transition by mode (3) was not observed for **10a**. As protons are most affected by temperature, imperceptible variations in hydrogen bonding might play a role. With abundant secondary interactions present in the supramolecule-assisted 3D network of NTHU-10, presumably, various types of passages of energy transfer were provided. But the transition might be somehow forbidden in **10a**, as its UV/Vis spectrum clearly showed little tendency to absorb in the visible region. On the other hand, UV spectra revealed that the tendency of energy absorption increased from **10b** to **10d**. Considering the progressively higher reaction temperatures from **10a** to **10d**, we assumed that certain local symmetry concealed in structure was temperature-dependent and gradually changed, thus turning forbidden transitions into allowed ones. As verification, bright-green emissive crystals of **10d** were found to be successfully formed from a sample of faint-blue fluorescent crystals of **10a** through hydrothermal heating.[23] The result also implied that **10a** to **10c** were metastable optical analogues relative to **10d**. As most hybrid materials would encounter partial quenching in emissions through cycles of heating and cooling, NTHU-10 is out of the ordinary and showed uncommon heat resistance in this respect. We observed that, after 60 % reduction in emission at 500 K, **10d** was able to resume its original capacity upon cooling to room temperature (Figure S4, S5 in the Supporting Information).

In conclusion, we have demonstrated that a highly innovative OMPO system (NTHU-10) showed extraordinary photoluminescence behavior resulting from three emission modes rarely found to coexist in hybrid materials. NTHU-10 may be considered as a potential green phosphor, as **10d** emitted strongly with a quantum yield of 11% (based on 90% for YAG:Ce),[24] much superior to most luminescent MOFs. The thorough study of the emission mechanism is exemplary in the metal-activator-free phosphor system. The unique combination of nanometer-sized 4R units of metal phosphate with organic linkers and template cations results in a robust supramolecular 3D network that showed extreme tolerance toward reaction temperatures. Normally a raise in temperature by 40 °C in the synthesis of hybrid porous materials can be high enough to produce different products or induce phase change.[9] Discovery of the four PL analogues with manifest variations in luminescence properties but no corresponding changes in structure or composition is unprecedented. The study with NTHU-10 sheds new light on conventional understanding of structure–property relationships and may offer new insights into future characterization for advanced materials. Moreover, the system of zinc phosphates incorporating aryl carboxylates seems to be rich, with diverse properties not seen to date in either MPOs or MOFs. Further investigation into the OMPO system for more new properties or potential applications is in progress.

Experimental Section

NTHU-10: The pure crystalline phase **10a** was obtained by heating a reaction mixture containing $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1 mmol), H_3PO_4 (0.27 mL, 4 mmol), benzene-1,2,4,5-tetracarboxylic acid (H_4btec; 0.127 g, 0.5 mmol)), 4,4′-bipyridine (bpy; 0.468 g, 3 mmol), and H_2O (10 mL, 555 mmol) in a 20 mL Teflon-lined autoclave for one day at 120 °C. Crystals of **10b**, **10c**, and **10d** were prepared under the same ratio of reactant mixture but at 160, 180, and 200 °C, respectively. Final products were all obtained as a single phase in 85–90% yield based on zinc.

CCDC 802477 (NTHU-**10a**) and 802478 (NTHU-**10d**) 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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[15] For a 2D MPO lattice connected by aryl carboxylate, see: Y. C. Liao, F. L. Liao, W. K. Chang, S. L. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 1320.

[16] Crystal data for **10a** and **10d**: $(C_{10}H_9N_2)[Zn(H_2PO_4)(C_{10}H_2O_8)_{0.5}]$, $Mr = 444.61$, monoclinic, space group $C2/c$, $Z = 8$; for **10a**, $a = 25.281(1)$, $b = 7.850(1)$, $c = 18.646(1)$ Å, $\beta = 116.333(1)°$, $V = 3316.6(2)$ Å^3; $R1 = 0.0224$ and $wR2 = 0.0616$; for **10d**, $a = 25.265(3)$, $b = 7.844(1)$, $c = 18.643(2)$ Å, $\beta = 116.385(2)°$, $V = 3309.6(7)$ Å^3, $R1 = 0.0216$ and $wR2 = 0.0642$.

[17] The samples for PL studies were loose powders (photos shown in the top of Figure 1), which were also used for PXRD, EA, and TGA measurements and for IR, Raman, and solid-state NMR spectroscopy. All PL spectra were recorded on a HORIBA Jobin Yvon Fluorolog-3 Spectro-fluorometer equipped with a Xe lamp (450 W) and Linkam THMS600 temperature-controlled stage (−196 to 600 °C).

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[21] Synthesis of K_4(btec): H_4btec (3 mmol) was added to H_2O (10 mL) to form an aqueous solution, which was then neutralized by $KOH_{(aq)}$ (3 mL, 4 M). The resulting solution was heated, and K_4(btec)was separated out as a solid precipitate.

[22] Synthesis of $[H_2bpy]Cl_2$: $HCl_{(aq)}$ (0.5 mL, 12 M) was added to a mixture of 4,4′-bipyridine (3 mmol) and H_2O (10 mL) and stirred for 3 h to make a homogeneous solution. Solid $[H_2bpy]Cl_2$ was obtained by evaporating water.

[23] After **10a** was produced, we placed the crystals together with the filtrate into an acid digestion bomb and heated them hydrothermally at 200 °C for one day. This treatment can transform **10a** into **10d**. Prolonged reaction time for **10a** at 120 °C or heating **10a** in solvent or in the solid state at 200 °C did not result in this transformation.

[24] The results from quantum yield measurements indicated that **10d** was the highest and **10c** the second (ca. 7%).