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From Stimuli-Responsive Polymorphic Organic Dye Crystals to Photoluminescent Cationic Open-Framework Metal Phosphate

Yu-Chuan Chang and Sue-Lein Wang*

Department of Chemistry, Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC

Supporting Information

ABSTRACT: Four photoluminescent dye crystals, TPB-*n* (*n* = 1−3) and TPCH, have been synthesized in isolation from carbon−carbon coupling of 4,4′-trimethylene-dipyridine (tmdp) in the absence of organic solvent and catalyst via in situ one-pot metal/ligand oxidative-dehydrogenation reactions. Large crystals have been obtained and readily separated from reaction products without the need for purification. Their structures were characterized: TPB and TPCH represent two dissimilar oxidized forms of tmdp dimers; TPCH was less oxidized but accompanied with partial hydrolysis with molecular formula further confirmed by FAB-MASS analysis. They exhibit distinct photoluminescence (PL) with quantum efficiency measured up to 42%. TPB-2 and TPB-3 are two polymorphic dihydrates, stimuli-responsive toward photoluminescence color changes; both can transform to TPB-1 upon gentle heating. Importantly, the three TPB-*n* crystals establish the first tetrapyridyl-type ligands adapted by metal phosphates to create a cationic luminescent framework, NTHU-12. This study serves as an inspiring route beyond conventional C−C bond formation reactions and has generated four tmdp dimers in isolation. The facile syntheses have resulted in ample production of a rare type of tetrapyridyl ligands, leading to the discovery of the first positively charged hybrid topology in nanoporous solids. The features of the four luminescent tmdp dimers and NTHU-12 embodied in synthesis, structure, and optical property are reported.

The synthesis of crystalline porous materials in the past decade has advanced substantially owing to the increasing demand for functional materials in applications involving molecular recognition, shape-selective catalysis, fluid separation, hydrogen gas storage, and solid-state lighting.[1] Two major categories of nanoporous structures have been under intensive investigations: one with purely inorganic frameworks such as silica-based zeolites,[2] germanates,[3] and phosphorus-based metal oxides (MPOs),[4] and the other with organic−inorganic hybrid frameworks like porous coordination polymers and metal−organic frameworks (MOFs).[5] Although the organic−inorganic hybrid structure of MOFs has attracted more attention by surpassing the inorganics in the aspect of controllable nature in syntheses as well as higher porosity and flexibility in structure, the inorganic open-frameworks of MPOs stand out in zeolite-like structures of variability and versatility. Beyond MPOs and MOFs, there in fact lies a hybrid field with rich structural chemistry, which may lead to new structure−property relationship. Very recently, important new optical and sorption properties have emerged from organo-metallophosphates (OMPOs). By mediating the pure inorganic MPO framework with the organic linker bdc (benzene dicarboxylate, used for MOF-5),[6] the first aryl carboxylate-incorporated MPO structure exhibiting unexpected bimodal porosity, NTHU-2, has been discovered in 2004,[7a] a milestone structure in OMPOs as it is still challenging to realize the synthesis of metal phosphates with aryl carboxylate-type ligands. Encouragingly, a second aryl carboxylate, benzene-1,2,4,5-tetracarboxylate (btec), has been successfully incorporated into MPO lattice to bring about two more interesting OMPOs, NTHU-8[7b] and NTHU-10.[7c] Besides bimodal porosity, they show further interesting hydrogen absorption and exciting optical properties. Moreover, in view of the structure, their frameworks reveal novel organic supramolecular assemblies and uncommon inorganic tectons rarely found in MPOs. Far beyond mixed traits of MPOs and MOFs, the system of OMPOs is full of potentiality for new materials and yet with little exploration in the realm of hybrid porous solids.

Amine-type porogens of high denticity are relatively few compared with the widely used bipyridine-type ligands in nanoporous structures. Recently, an interesting tetradentate amine, TPB (1,2,4,5-tetra(4-pyridyl) benzene), has been reported to emerge from carbon−carbon coupling of 4,4′-trimethylene-dipyridine (tmdp) through in situ metal/ligand reactions.[8] Notice that no organic reaction concerning the coupling reaction of tmdp to synthesize TPB has ever been reported.[9] But the single substance is not accessible unless those as-prepared TPB-MOF structures are demetallized to release TPB.[8b,c] Tetrapyridal-type ligands are rare, especially those capable of enduring hydrothermal conditions. It would be of great importance, therefore, to advance in situ metal/ligand reactions to achieve a direct synthesis of pure TPB substance for exploring new OMPO or MOF materials. Herein, we report the first facile synthesis of pure molecular solids of TPB, with an in-depth extensive exploration of four dimeric tmdp crystals (Figure 1). The three TPB dye crystals are appealing stimuli-responsive materials. They are the first tetrapyridyl-type ligands adaptable to metal phosphates, leading to the synthesis of a highly innovative OMPO structure, $(H_2btec)[Zn_2(H_2PO_4)_2(TPB)]$ (designated as NTHU-12, where btec

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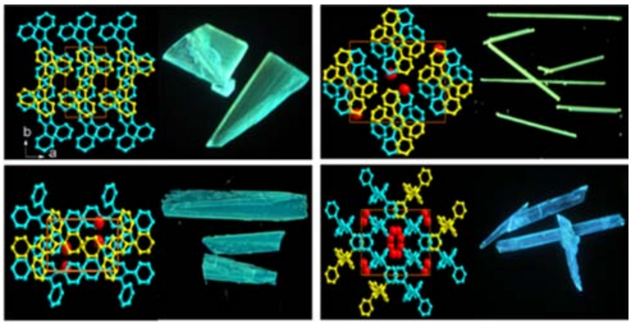
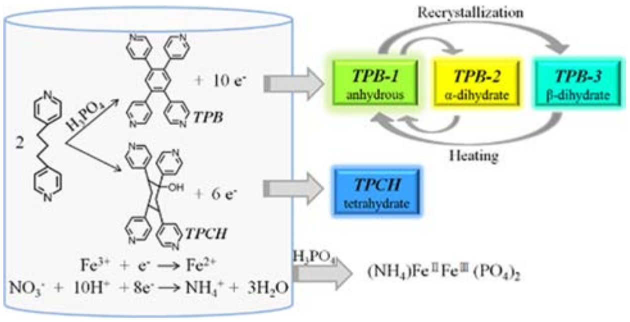


Figure 1. Molecular packing (projection down to c axis) and crystals under long UV light (λ = 365 nm): (a) TPB-1; (b) TPB-2; (c) TPB-3; and (d) TPCH. Molecules in yellow are in upper layer and cyan in bottom. The red balls are lattice water molecules.

= benzene-1,2,4,5-tetracarboxylate), in which negatively charged polycarboxylates uncommonly act as templates and the open-framework carries positive charge, a rarely encountered case in hybrid porous solids.

Three photoluminescent dye crystals, $C_{26}H_{18}N_4$ (TPB-1), α-$C_{26}H_{18}N_4{\cdot}2H_2O$ (TPB-2), and β-$C_{26}H_{18}N_4{\cdot}2H_2O$ (TPB-3) (see Table S1 for crystal data), originally emerged from the reactions for preparing iron analogue of an activator-free yellow phosphor gallium oxalatophosphate.[1e] TPB-1 is a unique anhydrous phase containing solely TPB molecules; TPB-2 and TPB-3 are both a dihydrate crystal, representing two polymorphs of TPB·$2H_2O$. All three were from direct coupling of tmdp in hydrothermal reactions[10] without using organic solvent and catalysts. Importantly, we employed $Fe(NO_3)_3$ and H_3PO_4, which were not mentioned in prior studies but were later identified as key reagents in the coupling of tmdp molecules (Scheme 1). Since the formation of one TPB molecule involves the release of 10 electrons, plenty oxidants are required to deplete them. We noticed that, in terms of the total amount of Fe^{3+} present in the reaction mixture, the reaction of Fe^{3+} to Fe^{2+} (one-electron reduction) seems not possible to digest all those electrons. A side product of $NH_4Fe_2(PO_4)_2$[11] caught our attention then: under the condition of no added ammonium in reactants, where was NH_4^+ from? The only possibility would be NO_3^- engaged in an 8-electron reduction reaction (Scheme 1), an important pathway of nitrate metabolism to produce fermentable N source for syntheses in cell growth. The exact oxidants and redox reactions concerning C−C coupling of tmdp molecules were previously vague but have now been clarified for the first time. We noticed that both metal and NO_3^- ions were oxidants, especially nitrate played a heavier role. Additionally, the presence of H_3PO_4 added a noticeable influence on the extent of oxidation by assisting the reduction of NO_3^- to NH_4^+ via forming $NH_4Fe_2(PO_4)_2$, indirectly facilitating the reaction for TPB. In the absence of H_3PO_4, no TPB crystals were produced. Instead, crystals of tetrahydrated TPCH (TPCH = 1-hydroxy-e,e,e,e-1,2,4,5-tetra(4-pyridyl) cyclohexane), began to emerge (Scheme 1 and Figure 1d). TPCH molecule is less oxidized than TPB and is the fourth dimeric form from tmdp molecules never reported before. Structure analysis revealed the TPCH molecules were residing on inversion centers with disordered OH groups, leading to the question about the exact number of OH groups per molecule. Later, with the molecular weight confirmed by FAB-MASS analysis (Figures S7), we attained the exactitude in the crystal structure of TPCH, and the molecular formula of TPCH has been confirmed without ambiguity.

Scheme 1. Oxidation and Reduction Reactions Involved in the Synthesis of Four Luminescent Dye Crystals by Direct C−C Coupling of tmdp Molecules, and Thermochromism in TPB-*n* Crystals



All four tmdp dimers are photoluminescent, arising from $\pi-\pi$ interactions between TPB molecules in solids. TPB-1 and TPB-2 are green and greenish-yellow phosphors with quantum efficiency of 39.5% and 42.3%, respectively; TPB-3 and TPCH are more toward blue with weaker emission intensity (Figure 2a). The differences in PL emission wavelengths and intensities may be due to dissimilarities in molecular packing and hydrogen bonding (Table S3). It is worth noting that, after gentle heating, both TPB-2 and TPB-3 could give green emission. From the results of PL emission spectra combined with powder X-ray diffraction analysis, we confirmed the heat-

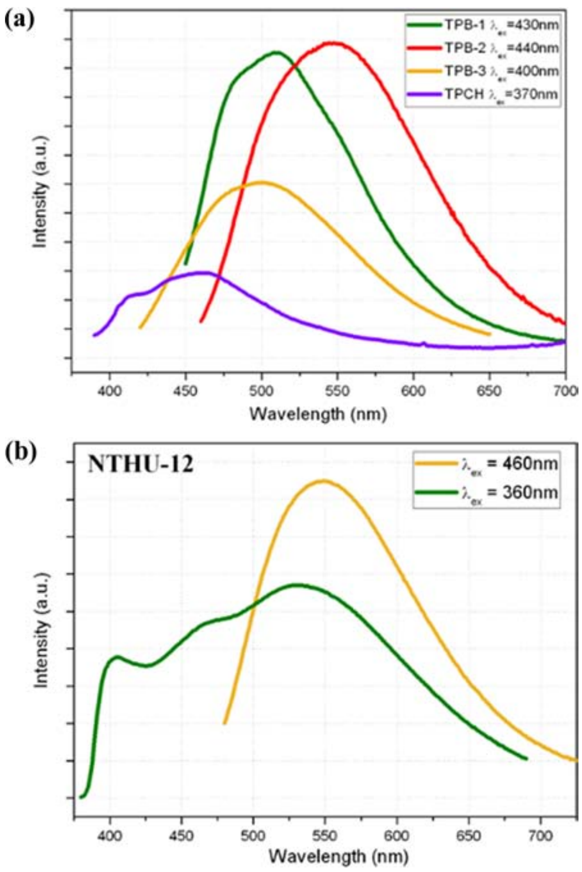


Figure 2. PL emission spectra measured from solid samples of tmdp dimers (a) and NTHU-12 (b).

treatment products of TPB-2 and TPB-3 had been transformed into the anhydrous phase of TPB-1. Reverse transformation from TPB-1 to the polymorpic TPB-2 or TPB-3 could be achieved through recrystallizing TPB-1 in ethanol.[12] Temperature-dependence PL spectra (Figure 3a) shows how the original greenish-yellow emission was shifting to the final green emission in the process of heating (conversion from TPB-2 into TPB-1), and heat-induced luminescence change occurred to TPB-2 (Figure 3b) implies that the three TPB crystals with such distinctive luminescent properties are potential sensor materials.[13]

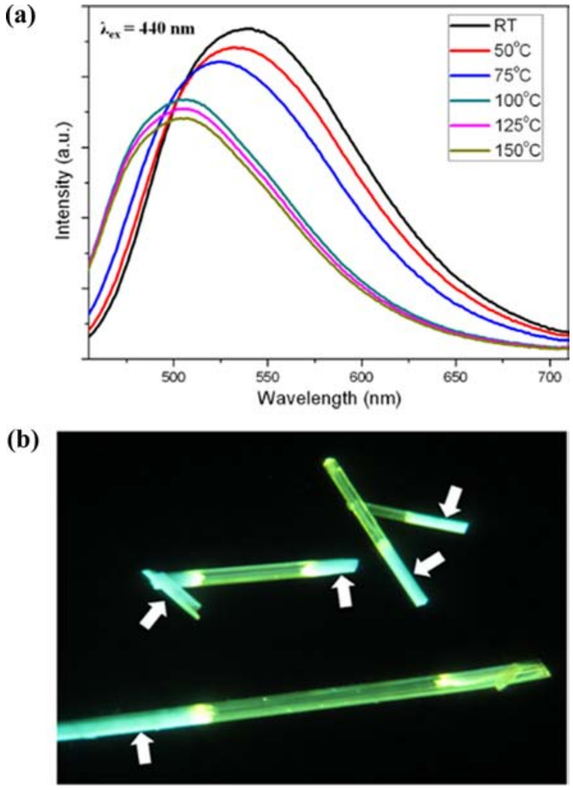


Figure 3. Temperature-dependence luminescence property: (a) PL spectra showed how the original greenish-yellow emission of TPB-2 was shifting to the green emission corresponding to that of TPB-1 in the process of heating; and (b) the photo revealed photoluminescence color change as one end (pointed by white arrows) was gently heated.

In the synthesis of NTHU-12, all three forms of TPB crystals provide equally good sources of TPB molecules.[14] The composition of the 3D network, built up with two kinds of tetrahedra, ZnO_2N_2 and H_2PO_4, and two independent TPB molecules (Figure 4a), was unambiguously determined from structure analysis[15] to be uncommonly positive-charged $[Zn_2(H_2PO_4)_2(TPB)]^+$. Cationic frameworks often occur to layered double hydroxides and polymetallic compounds.[16] To the best of our knowledge, there have been no such examples in hybrid structures. The inorganic skeleton of NTHU-12 comprises arrays of infinite $[ZnH_2PO_4]$ chains (Figure S10) running along *a*-axis. Isolated single tetrahedral chains are rare.[17] The zigzag-shaped $[ZnH_2PO_4]$ chains are linked by tetradentate TPB ligands into rectangular-packing arrays perpendicular to *bc* plane. As viewed along the *c*-axis direction, tunnels with openings of 8.1 × 9.3 Å were observed between each adjacent pair of inorganic chains. Negatively charged template $(H_2btec)^{2-}$ ions were residing within the channels to balance the framework charge. The $(H_2btec)^{2-}$ anions were closely aligned alongside the single zigzag inorganic chains (Figure 4b). There were strong hydrogen bonds between H_2PO_4 unit of the chain and C═O group of the template ($d_{CO\cdots OP}$ = 2.55, 2.74 Å, Table S3). Unlike NTHU-8[7b] and NTHU-10[7c] with four carboxylate groups sticking out of molecular planes, NTHU-12 has all the $(H_2btec)^{2-}$ ions in nearly perfect-planar shape. Between TPB ligands and $(H_2btec)^{2-}$ templates aligning along the *b*-axis, face-to-face $\pi-\pi$ interactions (3.68 Å) were observed. Consequently, an interesting acid−base-acid type of supramolecular trimer, $[(H_2btec)^{\cdots}TPB^{\cdots}(H_2btec)]$, was identified within NTHU-12. The organic supramolecular clusters endow NTHU-12 remarkable luminescence properties: near-white light from triple-wavelength emissions under the excitation of long UV light (λ_{ex} = 360 nm) and yellow light from a single emission centered at 550 nm under blue-light excitation (λ_{ex} = 460 nm) (Figure 2b).

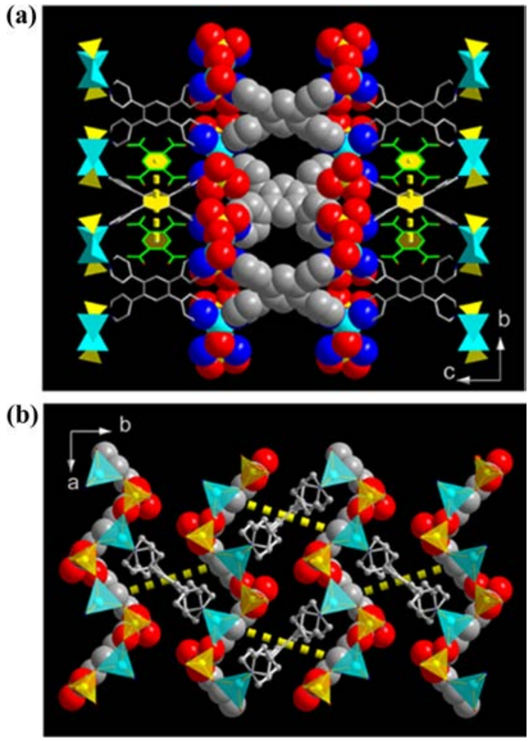


Figure 4. The 3D framework structure of NTHU-12: (a) negatively charged template (in green) and $\pi-\pi$ interactions (yellow dashed lines) between template and ligand (in gray) and supramolecular trimers; (b) the zigzag infinite $[ZnH_2PO_4]$ chains and templates closely aligned alongside. Tetrahedra of Zn in cyan, P in yellow; balls in gray are C atoms, blue N atoms, and red O atoms.

In conclusion, this study provides a new gateway in the synthesis of rare tetrapyridal dye crystals, from which an innovative OMPO topology with positively charged hybrid open-framework in nanoporous solids was discovered for the first time. The tetrapyridal molecules, TBP and TPCH, have never been reported to be directly synthesized through C−C coupling of tmdp molecules. We have shown a fundamentally inspiring effectual route to C−C bond formation without organic solvents and catalysts and achieved direct coupling of tmdp molecules into four luminescent dye crystals under hydrothermal conditions. We have ascribed the success to the amazing phosphate-assisted reduction of nitrate shown in

Scheme 1. Contrary to the roles normally played by arylcarboxylates and amines, NTHU-12 demonstrates a structure distinct to all prior OMPOs with reversed roles: templates played by arylcarboxylates and ligands by amines. With the tetradentate TPB ligand, a rare single tetrahedral MPO chain emerged and a novel topology beyond pillared-layer type with pyridine-type ligands often resulted. NTHU-12 exhibits significant structure features and optical properties new to both MPOs and MOFs. The cationic feature of the hybrid framework is unique, and may provide a sufficient ground for sensor materials especially when combined with its luminescent property.[18] The search for more OMPO topologies and new properties with the use of tetrapyridal ligands is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data and structure refinement tables, EA, FAB-MASS, TGA curves, crystal photos and plots for the structure, temperature-dependent powder diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

slwang@mx.nthu.edu.tw

Notes

The authors declare no competing financial interest.

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(9) Organic reactions ever concerning TPB was reported to prepare from pyridine molecules. See Fujita, M.; Oka, H.; Ogura, K. *Tetrahedron Lett.* **1995**, *36*, 5247−5250.

(10) Large TPB-*n* crystals (Figure S1) were obtained by hydrothermal heating a mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (0.161 g, 0.4 mmol), H_3PO_4 (0.6 mL, 9 mmol), tmdp (1.268 g, 6.4 mmol), oxalic acid dihydrate (0.151 g, 1.2 mmol), and water (2 or 10 mL) at 180 °C for 48 h. From the reaction with 2 mL of water, the product contained TPB-1 (a minor phase) and TPB-2 (a major phase with yield up to 35% based on tmdp), and with 10 mL of water, the product contained TPB-3 (yield ~30%). In both reaction products, we found $NH_4Fe_2(PO_4)_2$ as a by product. Large TPCH crystals (in ~ 30% yield) were obtained from the above reaction mixture for preparing TPB-3 but not including H_3PO_4.

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(12) Recrystallization of TPB-1 in 95% ethanol would result in TPB-2 only. If the process involved additional water, it would result in a mixture of TPB-2 and TPB-3.

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(14) Pale-yellow transparent crystals of NTHU-12 were obtained by heating a mixture of $Zn(acetate)_2 \cdot 2H_2O$, H_3PO_4, benzene-1,2,4,5-tetracarboxylic acid (H_4btec), TPB (from TPB-1, TPB-2 or TPB-3), and H_2O with the molar ratio of 1:4:0.4:0.4:555 under a mild hydrothermal conditions at 140 °C for 48 h; reaction yield was ~ 45%.

(15) Crystal data for NTHU-12: $(H_2btec)[Zn_2(H_2PO_4)_2(TPB)]$ M_r = 963.32, Orthorhombic, space group *Pnnm*, a = 9.2671(5) Å, b = 17.1198(9) Å, c = 24.841(1) Å, V = 3941.1(4) Å^3, Z = 4; R1 = 0.0485 and wR2 = 0.1259.

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