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Charge Effect of Foreign Metal Ions and Crystal Growth Process in Hybridized Metal-Organic Frameworks

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Experimental Details

Preparations. The organic material H₃TPO was prepared by using the literature method.\textsuperscript{11}

[Cu(HTPO)](DMF)₂(H₂O)₁₅ (CuHTPO; 1): H₃TPO (100 mg, 0.24 mmol), Cu(NO₃)₂·6H₂O (88 mg, 0.37 mmol), 5 mL of mixed solvent (DMF:H₂O:MeOH=3:3:1), and a few amount of HNO₃ were located together in a 10 mL vial. The vial was sealed tightly and placed in a preheated oven at 70 °C. After 48 h, green crystals precipitated. The crystals were separated by filtration and washed with mixed solvent (DMF:H₂O:MeOH = 3:3:1). Yield: 85%. Elemental analysis (%) calcd for C₂₇H₃₀CuN₂O₁₀.5P: C 50.27, H 4.69, N, 4.34; found: C 50.53, H 4.23, N 4.12.

ZnTPO/CuHTPO: CuHTPO (20 mg, 0.031 mmol), Zn(NO₃)₂·6H₂O (149 mg, 0.5 mmol), and 1 mL of mixed solvent (DMF:H₂O:MeOH = 3:3:1) were put together in a 10 mL vial. The sealed vial was located in an oven at 100 °C. After 72 h, core-shell type crystals were formed. The crystals were filtered and washed with mixed solvent (DMF:H₂O:MeOH = 3:3:1). The shell crystal was carefully cut to collect single-crystal X-ray diffraction data and analyzed as (H₃O)₂[Zn₃(TPO)₄(OH)_6(O)] (ZnTPO; 2). The structure with a chemical formula of H[(Zn₃(OH))(H₂O)_₃(TPO)_₂], reported in the literature,\textsuperscript{12} was afforded by using the same experimental conditions in the absence of CuHTPO.

TbTPO/CuHTPO: CuHTPO (20 mg, 0.031 mmol) and Tb(NO₃)₃·5H₂O (218 mg, 0.24 mmol) were put in a 10 mL vial (1 mL mixed solvent of DMF:H₂O:MeOH=3:3:1). The vial was sealed tightly and located in a preheated oven at 100 °C. After 72 h, core-shell crystals were formed. The crystals were collected by filtration and washed with mixed solvent (DMF:H₂O:MeOH = 3:3:1). The shell part, (H₂O)[Tb₂(TPO)₂(formate)] (TbTPO; 3), was carefully cut to study single-crystal X-ray diffractions. The Tb complex was alternatively prepared as a following method: H₃TPO (100 mg, 0.24 mmol), Tb(NO₃)₃·5H₂O (104 mg, 0.24 mmol) were placed in 5 mL of mixed solvent
(DMF:H₂O:MeOH = 3:3:1), and a few amount of HNO₃ were located together in a 10 mL vial. The sealed vial was put in a preheated oven at 100 °C. After 24 h, block shaped colorless crystals were produced. The crystals were isolated by filtration and washed with mixed solvent (DMF:H₂O:MeOH = 3:3:1). Yield: 70%. Elemental analysis (%) calcd for C_{55.8}H_{59.8}N_{2.3}O_{22.4}P_{2}Sb₂: C 43.79, H 3.95, N 3.86; found: C 43.30, H 4.58, N 4.23.

Crystallographic Structure Determination. X-ray data for 1 - 3 were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). Preliminary orientation matrix and cell parameters were determined from three sets of φ scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures of 1 – 3 were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. Guest molecules in 1 - 3 are significantly disordered and could not be modeled properly, thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. For 1, the contributions of some 548 electrons were removed from the unit-cell contents, and as Z = 8 in this case, this could/might correspond with the removal of solvent such as 1(DMF) and 3(H₂O) [some 69 electrons] from the Cu(II) formula unit. For 2, the contributions of some 1259 electrons were removed from the unit-cell contents. The oxygen (O4) atom is at a site with -3 symmetry and there are six Zn(II)₁₂₃ formula units in the unit cell. Therefore, this could/might correspond with the removal of solvent such as 5(DMF) and 1(H₂O) [some 210 electrons] from the Zn(II)₁₂₃ formula unit. The water and carboxylate oxygens were disordered over two sites (0.61:0.39 for O₈A and O₈B, 0.5:0.5 for O₉A and O₉B), respectively. For 3, the contributions of some 199 electrons were removed from the unit-cell contents, and as Z = 2 in this case, this could/might correspond with the removal of solvent such as 2(DMF) and 2(H₂O) [some 100 electrons] from the Tb(III)₁₂₃ formula unit. All hydrogen atoms except for hydrogens bound to water oxygen were calculated at idealized positions and refined with the riding models. Crystal data of 1(squeezed): empirical formula = C_{23.88}H_{38.9}CuNO_{1.1}P, Mr = 597.47, T = 130 K, orthorhombic, space group Pbcn, a = 16.0811(4) Å, \( b = 24.0918(6) \) Å, \( c = 14.2992(4) \) Å, \( V = 5539.8(2) \) Å³, Z = 8, \( D_{calc} = 1.433 \) g cm⁻³, \( \mu = 0.904 \) mm⁻¹, 83887 reflections collected, 6858 unique (\( R_{int} = 0.0536 \)), \( R1 = 0.0438 \), \( wR2 = 0.1332 \) \( [I > 2\sigma(I)] \). 2(squeezed): empirical formula = C_{25.8}H_{38.9}N_{13.3}O_{12.9}P_{9}Zn_{15}, Mr = 6964.76, T = 100 K, trigonal, space group R-3, \( a = 34.340(3) \) Å, \( c = 19.451(2) \) Å, \( V = 19865(4) \) Å³, Z = 3, \( D_{calc} = 1.747 \) g cm⁻³, \( \mu = 1.493 \) mm⁻¹, 27880 reflections collected, 10904 unique (\( R_{int} = 0.0935 \)), \( R1 = 0.0792 \), \( wR2 = 0.2103 \) \( [I > 2\sigma(I)] \). 3(squeezed): empirical formula = C_{6}H_{24.5}N_{12.2}P_{9}Tb_{2}, Mr = 1377.15, \( T = 296 \) K, monoclinic, space group \( P2/n \), \( a = 14.4794(6) \) Å, \( b = 10.5573(5) \) Å, \( c = 23.3160(11) \) Å, \( \beta = 107.316(3) \), \( V = 3402.6(3) \) Å³, Z = 2, \( D_{calc} = 1.344 \) g cm⁻³, \( \mu = 2.171 \) mm⁻¹, 28623 reflections collected, 8407 unique (\( R_{int} = 0.0664 \)), \( R1 = 0.0447 \), \( wR2 = 0.1007 \) \( [I > 2\sigma(I)] \).

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer.
Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min in a N₂ flow using a Scinco TGA N-1000 instrument. PXRD data were recorded using Cu Kα (λ = 1.5406 Å) on a Rigaku Ultima III diffractometer with a scan speed of 2°/min and a step size of 0.01°. Photoluminescence were measured with a Hitachi F-7000 FL spectrophotometer. The ICP data were collected on ICP-AES (ICP-OES; JY Ultima2C; Jobin Yvon, France) spectrometer.

**Gas Sorption Measurements.** Gas sorption isotherms were measured using a BEL Belsorp mini II gas adsorption instrument up to 1 atm of gas pressure. The desolvated sample 1 was obtained by heating CuHTPO at 160 °C under vacuum for 16 h. The highly pure N₂ (99.999%), H₂ (99.999%), CO₂ (99.999%), CH₄ (99.995 %), CO (99.998%), and O₂ (99.995%) were used in the sorption experiments. N₂ and H₂ gas isotherms were measured at 77 K and CO₂ was measured at 195 K. For H₂, the additional uptake isotherm was obtained at 87 K to calculate heats of adsorption.

**References**

s3. G. M. Sheldrick, 1994, SADABS, A program for area detector absorption corrections, University of Göttingen, Germany.
Fig. S1. (top) Structure of H$_3$TPO and (bottom) molecular view showing the geometric environment around the Cu$_2$(CO)$_4$ SBU of CuHTPO.
Fig. S2. Structure of dimeric (HTPO)$_2$ unit through hydrogen bonding in CuHTPO.

Fig. S3. Three-dimensional network of CuHTPO in the $bc$ plane.
Fig. S4. Connolly surface diagram with 1D channels running down the a-axis.
Fig. S5. Simplified net of CuHTPO.
Fig. S6. TGA data for CuHTPO. A weight loss of 24% in thermogravimetric analysis (TGA) on CuHTPO corresponds to removal of 0.5 H$_2$O and 2 DMF molecules in the temperature range of 27 – 300 °C. The framework remains intact up to 310 °C.

Fig. S7. PXRD profiles with indicated temperatures for CuHTPO. The framework integrity up to 310 °C was confirmed by the variable temperature PXRD data.
Fig. S8. PXRD profiles for simulated, CuHTPO, desolvated CuHTPO at 160 and 200 °C under vacuum for 16 h. The structural integrity is retained at both conditions.

Fig. S9. N$_2$ sorption isotherms of desolvated CuHTPO activated at different temperatures. The adsorption capacity is almost same at the two temperatures. The structural integrity is retained at both conditions with identical sorption capacity.
Fig. S10. Adsorption isotherms of desolvated CuHTPO with several gas molecules. Permanent microporosity is verified by measuring the N$_2$ sorption isotherm for CuHTPO, which shows a characteristic type I curve. From this plot, the Brunauer-Emmett-Teller (BET) surface area and total pore volume are extracted to be 950 m$^2$/g and 0.38 cm$^3$/g, respectively. For H$_2$ and CO$_2$ uptake, the maximum amounts at 1 atm and 77 K are equal to 8.57 mmol/g (192 cm$^3$/g) and 10.1 mmol/g (226 cm$^3$/g), which are equivalent to the number of gas molecules per formula unit being 4.0 and 4.8, respectively.
Fig. S11. (a) H₂ isotherms at 77 K and 87 K, and virial equation fits for desolvated CuHTPO. (b) Plot of the isosteric heat of H₂ adsorption for desolvated CuHTPO.

The H₂ adsorption data at two temperatures were fitted using the virial-type equation with $a_i$ and $b_i$ parameters,

$$\ln P = \ln N + \left(\frac{1}{T}\right)\sum_{i=0}^{r}(a_iN^i) + \sum_{i=0}^{s}(b_iN^i)$$  \hspace{1cm} (1)

where $P$ is the pressure in Torr, $N$ is the amount adsorbed in mmol/g, $T$ is the temperature in K, $a_i$ and $b_i$ are virial coefficients, and $r$ and $s$ are the number of coefficients required to express the isotherms. The fitted coefficients $a_0$ through $a_r$ were then applied to estimate the isosteric heat of adsorption using the following expression

$$Q_{st} = -R\sum_{i=0}^{r}(a_iN^i)$$  \hspace{1cm} (2)

where $Q_{st}$ is the isosteric heat of adsorption depending on the coverage and $R$ is the universal gas constant.

The data were fitted with a virial-type equation to give the adsorption enthalpy of 6.3 – 6.4 kJ/mol. This value is analogous to those of metal-carboxylate or metal-cyanide MOFs.\textsuperscript{7}

Fig. S12. Several gas isotherms of the desolvated CuHTPO at 273 K. The uptake ratios of CO$_2$ over the other gases at 1 atm are 3.2 for CO$_2$/CH$_4$, 8.9 for CO$_2$/CO, 13.4 for CO$_2$/N$_2$ and CO$_2$/O$_2$, and 107.1 for CO$_2$/H$_2$. The higher capacity of CO$_2$ is related to the greater quadrupole moment and polarizability of CO$_2$ compared to the other gas molecules.
Fig. S13. Building nodes of a) Zn₄(OH)₃(H₂O)₂(TPO)₈ and b) Zn₃(O)(TPO)₈ for ZnTPO. Zn and carboxylate oxygens are disordered. c) Extended 3D view in the ab plane.
Fig. S14. Simplified net of ZnTPO.
Fig. S15. a) Building unit of Tb₂(formate)(TPO)₄ for TbTPO. b) Extend structural view in the ac plane.
Fig. S16. Simplified net of TbTPO.
Fig. S17. PXRD profiles of (a) ZnTPO/CuHTPO and (b) TbTPO/CuHTPO crystals.
Fig. S18. (a) (left) Solution of 0.5 M Zn(NO$_3$)$_2$ in DMF:H$_2$O:MeOH. (right) Filtrate after a solvothermal reaction of CuHTPO and Zn$^{2+}$ in DMF/H$_2$O/MeOH. (b) (left) Solution of 0.5 M Tb(NO$_3$)$_3$ in DMF/H$_2$O/MeOH. (right) Filtrate after a solvothermal reaction of CuHTPO and Tb$^{3+}$ in DMF/H$_2$O/MeOH.
Fig. S19. IR data of (a) the filtered solution of ZnTPO/CuHPTPO reaction mixture, Cu(NO$_3$)$_2$, and H$_3$TPO, and (b) the filtered solution of TbTPO/CuHPTPO reaction mixture, Cu(NO$_3$)$_2$, and H$_3$TPO.
Fig. S20. UV/Vis spectra of CuHTPO in mixed solvent and Cu$^{2+}$ solution.
Fig. S21. Proposed growth mechanism for the hybridized systems.
Fig. S22. Magnified photographs of (a) as-synthesized CuHTPO crystals, (b) CuHTPO crystals in the K⁺ solution, and (c) CuHTPO crystals in the Na⁺ solution.

Fig. S23. Photographs of CuHTPO crystals in the vials after CuHTPO crystals were treated in the K⁺ and Na⁺ solution under solvothermal conditions for 100 h.
Fig. S24. Magnified photographs of CuHTPO crystals immersed in a DMF solution of Zr$^{4+}$ under solvothermal conditions. Most of the CuHTPO crystals were collapsed and disappeared at t = 60 min.
Fig. S25. TGA data for **TbTPO**, showing that the solvent molecules were removed at 240 °C and the framework was stable up to 520 °C, above which **TbTPO** started to decompose. Based on the thermal stability, the **TbTPO** sample was activated at 250 °C under vacuum for 18 h.

![TGA graph](image)

Fig. S26. PXRD profiles for simulated, as-synthesized, and desolvated **TbTPO** at 250 °C. The structural integrity of the desolvated **TbTPO** was maintained, as checked by PXRD data in which the patterns of the as-prepared and desolvated samples are quite similar.

![PXRD profiles](image)
Fig. S27. Adsorption isotherms of desolvated TbTPO with several gas molecules. The N₂ isotherm of the evacuated TbTPO indicates a normal type I characteristic, which proves permanent porosity of TbTPO. The BET surface area and total pore volume are estimated to be 834 m²/g and 0.35 cm³/g, respectively. The H₂ uptake at 1 atm and 77 K reaches 6.96 mmol/g (156 cm³/g) and the number of gas molecules per formula unit is calculated to be 8.3.
Fig. S28. (a) H\textsubscript{2} isotherms at 77 K and 87 K, and virial equation fits for desolvated Tb\textsuperscript{3+}TPO. (b) Plot of the isosteric heat of H\textsubscript{2} adsorption for desolvated Tb\textsuperscript{3+}TPO. The isosteric heat of adsorption for H\textsubscript{2} is in the range of 6.3 – 6.5 kJ/mol, which is similar to those of TPO-containing lanthanide MOFs.\textsuperscript{s8}

Fig. S29. Emission spectrum for **TbTPO**. The Tb emission peaks were assigned. This gives rise to the strong green luminescence. The characteristic peaks can be assigned to $^5D_4 \rightarrow ^7F_j$ transitions.

Fig. S30. Emission spectra for **H$_3$TPO** (dashed line) and **TbTPO/CuHTPO** at 60 h (solid line). The Tb emission peaks were assigned. The emission profile shows typical Tb$^{3+}$ peaks, which are identical to those of **TbTPO**.
Fig. S31. Emission spectra for H₃TPO and ZnTPO/CuHTPO at 60 h. In the case of ZnTPO/CuHTPO, the luminescence can only arise from ZnTPO because paramagnetic Cu²⁺ can quench or reabsorb the emission of CuHTPO.