Supporting information for

Temperature-dependent Supramolecular Isomerism in Three Zinc Coordination Polymers with Pamoic Acid and 1,4-Bis(imidazol-1-ylmethyl)-benzene

Suna Wang*[a,b] , Yanqiang Peng[a], Xilian Wei[a], Qingfu Zhang[a], Daqi Wang[a], Jianmin Dou[a], Dacheng Li[a], Junfeng Bai [b*]

Experimental:

General Methods:

H_2PA was purchased from Alfa-aesar. Bix was synthesized according to previous literature [1]. Other reagents were commercially available and used as purchased without further purification. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000-400cm^{-1} on a VECTOR 22 spectrometer. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 700 °C with a heating rate of 10°C/min under flowing nitrogen. The emission/excitation spectra were recorded on a Hitachi 850 fluorescence spectrophotometer. Preliminary Kurtz powder second harmonic generation (SHG) measurements were carried out using the using the 1064 nm fundamental wavelength from a Nd: YAG laser.

Synthesis of the complexes.

Synthesis of $[Zn(PA)(bix)]_n$ (*α*):

A mixture of pamoic acid (38.8 mg, 0.10 mmol), bix (27.6 mg, 0.15 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (25.1g, 0.1mmol) in mixed solvents CH_3OH/DMF (3mL/5mL) was placed in a Parr Teflon-lined stainless steel vessel and heated to 120ºC for 48h. Then the reaction system was cooled to room temperature slowly, and colorless block crystals of ***α*** were obtained. After filtration, the crystals were washed with water and dried in air (0.024 g, yield 60% based on PA). $C_{37}H_{28}N_4O_6Zn$ (690.00): calcd. C 64.35, H 4.06, N 8.12; found C 64.13, H 4.01, N 8.20. IR (KBr pellet): 3436(br, m), 3130(m), 3056(w), 2930(w), 1667(s), 1559(m), 1509(m), 1454(s), 1391(vs), 1351(s), 1331(s), 1236(m), 1091(m), 952(w), 750(m), 657(w) cm^{-1}.

Synthesis of $\{[Zn(PA)(bix)]\cdot 2DMF\}_n$ (*β*)

Similar procedures were performed, except that the reaction temperature was 100 ºC. The reaction system was cooled to room temperature to give colorless block crystals of ***β*** which were filtrated, washed with water and dried in air (0.022g yield 37% based on H_2PA). $C_{43}H_{42}N_6O_8Zn$ (836.20): calcd. C 61.70, H 5.02, N 10.04; found C 61.58, H 5.12, N 10.13. IR (KBr pellet): 3437(m), 3126(s), 3051(w), 2492(w), 2789(w), 1639(m), 1559(m), 1508(m), 1451(m), 1388(vs), 1350(m), 1310(m), 1234(m), 1090(m), 953(w), 834(w), 763(m), 655(w)cm^{-1}. In fact, similar reactions in the temperature range 70-110 ºC all afford such complex.

Synthesis of $\{[Zn(PA)(bix)]\cdot 3.7DMF\}_n$ (*γ*)

Two different methods both afford ***γ*** phase, with different amounts of ***β*** mixed while no pure ***γ*** phase was obtained.

Method 1: Similar procedures were performed as those of ***α*** and ***β***, except that the reaction temperature was 60 ºC.

Method 2: A solution of bix (27.6 mg, 0.15 mmol) in CH_3OH (3 mL) was carefully layered on a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (25.1g, 0.1mmol) and pamoic acid (38.8 mg, 0.10 mmol) in DMF (3 ml). Colorless crystals were obtained in a few days.

Synthesis of unknown phase at 0 ºC.

A solution of bix (27.6 mg, 0.15 mmol) in CH_3OH (3 mL) was carefully layered on a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (25.1g, 0.1mmol) and pamoic acid (38.8 mg, 0.10 mmol) in DMF (3 ml). Then the reaction system was put into the refrigerator with the temperature fixed at 0 ºC**.** Colorless crystals were obtained in a few days. Due to the poor crystalline and stability of the product, no single crystals for X-ray diffraction were obtained.

X-ray Crystallography:

Suitable single crystals were selected for indexing and intensity data were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. The raw data frames were intergrated into SHELX-format reflection files and corrected using SAINT program. Absorption corrections based on multiscan were obtained by the SADABS program. The structures were solved with direct methods and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively [2]. The coordinates of the non-hydrogen atoms were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Selected bond lengths and angles of these complexes are listed in Table S1. CCDC 806030-806032 for **α**-**γ** 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.

In ***β***, the lattice DMF molecules are disordered. All the atoms of one DMF are disordered over two general positions (C38/C38’, C39/C39’, C40/C40’, O7/O7’, N5/N5’) which were refined isotropically with a site-of-occupancy of 0.606(6)/0.394(6). The atoms of the other DMF molecule (C41/C41’, C42/C42’, C43/C43’, O8/O8’, N6/N6’) are also disordered over two general positions and refined isotropically with a site-of-occupy of 0.727(7)/0.273(7). In ***γ***, the solvent molecules are highly disordered, and attempts to locate and refine them were unsuccessful. The SQUEEZE program was used to remove scattering from the highly disordered solvent molecules and a new .HKL file was generated. The structure was solved by using the new generated .HKL file. Structure refinement after modification of the data with the SQUEEZE [3] routine led to better refinement and data convergence: R1 = 0.0623, wR2 = 0.0975.

References:

[1] B. F. Hoskins, R. Robson, D. A. Slizys, J. Am. Chem. Soc. 119 (1997) 2952.

[2] Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Göttingen University: Göttingen, Germany, **1997**; Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, **1997**

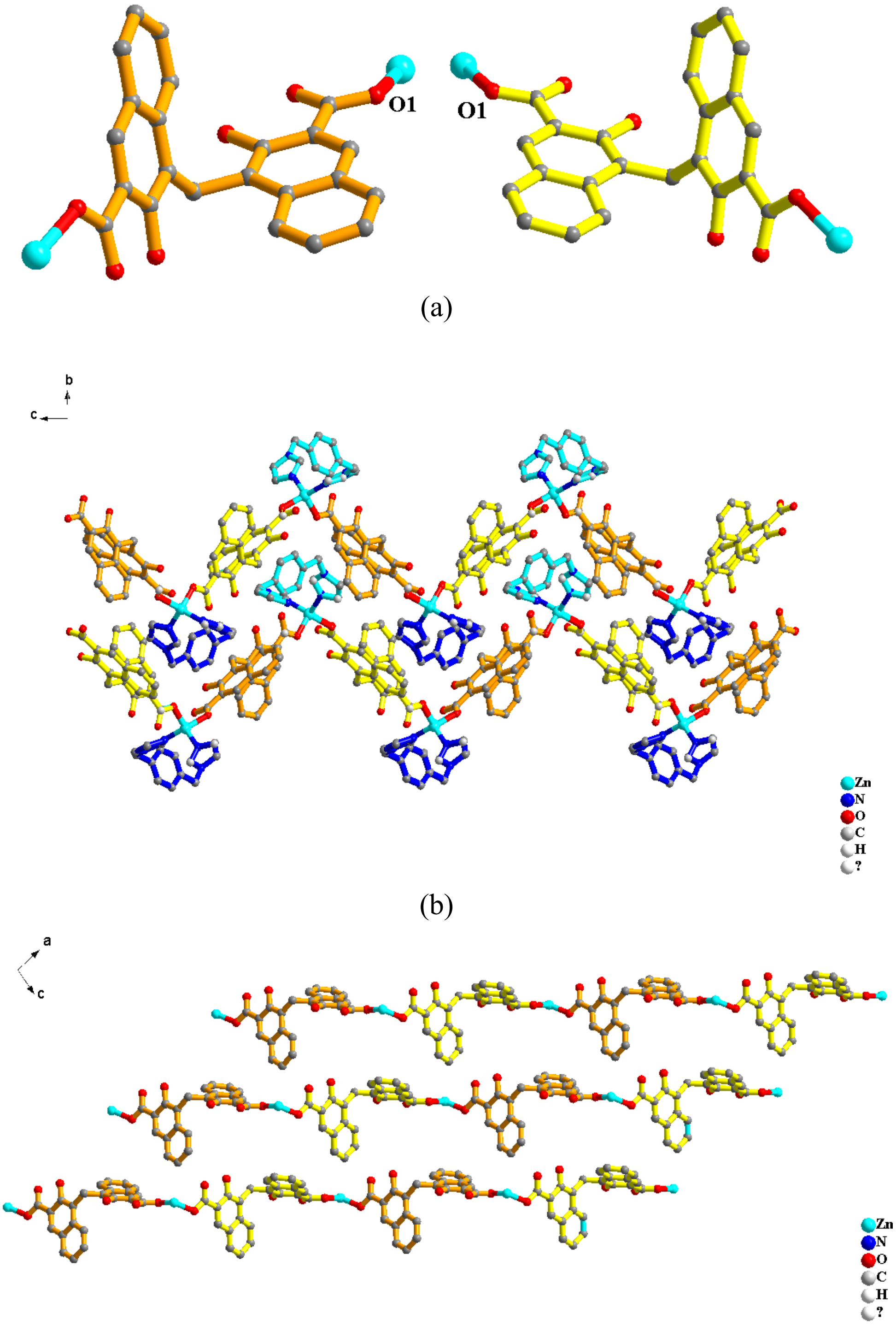
[3] Spek, A. L. (2003), J. Appl. Cryst. 36, 7.

Table S1. Selected bond length and angles in the complexes.

		α	
Zn(1)-O(5A)	1.956(2)	Zn(1)-O(1)	1.966(3)
Zn(1)-N(3B)	1.993(3)	Zn(1)-N(1)	2.002(3)
O(5A)-Zn(1)-O(1)	100.26(11)	O(5A)-Zn(1)-N(3B)	128.08(11)
O(1)-Zn(1)-N(3B)	103.67(11)	O(5A)-Zn(1)-N(1)	100.16(11)
O(1)-Zn(1)-N(1)	114.67(11)	N(3B)-Zn(1)-N(1)	110.18(13)
		β	
Zn(1)-O(5A)	1.934(3)	Zn(1)-O(1)	1.957(3)
Zn(1)-N(1)	1.986(3)	Zn(1)-N(3B)	2.024(4)
O(5A)-Zn(1)-O(1)	105.96(13)	O(5A)-Zn(1)-N(1)	128.46(14)
O(1)-Zn(1)-N(1)	114.16(13)	O(5A)-Zn(1)-N(3B)	101.75(13)
O(1)-Zn(1)-N(3B)	97.59(14)	N(1)-Zn(1)-N(3B)	103.52(14)
		γ	
Zn(1)-N(1)	1.928(6)	Zn(1)-O(1)	1.943(4)
Zn(1)-N(3A)	1.944(6)	Zn(1)-O(4B)	1.960(6)
N(1)-Zn(1)-O(1)	123.4(2)	N(1)-Zn(1)-N(3A)	108.9(2)
O(1)-Zn(1)-N(3A)	103.4(2)	N(1)-Zn(1)-O(4B)	108.9(2)
O(1)-Zn(1)-O(4B)	111.3(2)	N(3A)-Zn(1)-O(4B)	97.8(2)

Symmetry codes: ***α***, A:x-1, -y+1/2, z-1/2; B:x-1, y, z; C:x+1, -y+1/2, z+1/2; D:x+1, y, z. ***β***, A:x-1/2, -y+1/2, z-1/2; B:-x+1/2, y-1/2, -z-1/2; C:-x+1/2, y+1/2, -z-1/2; D:x+1/2, -y+1/2, z+1/2. ***γ***, A:-x+2, y+1/2, -z+3/2; B:-x+1/2, -y+1, z+1/2; C:-x+2, y-1/2, -z+3/2; D:-x+1/2, -y+1, z-1/2.

Fig. S1. View of the two glide-plane related conformation of the PA^{2-} ligand in ***α*** (a) and their arrangement in the three-dimensional supramolecular structure along *a* axis (b) as well as in the monolayer along *ac* plane (c), respectively. Two mirror-related conformations were in orange and yellow. In (c), bix ligands were omitted for clarity.

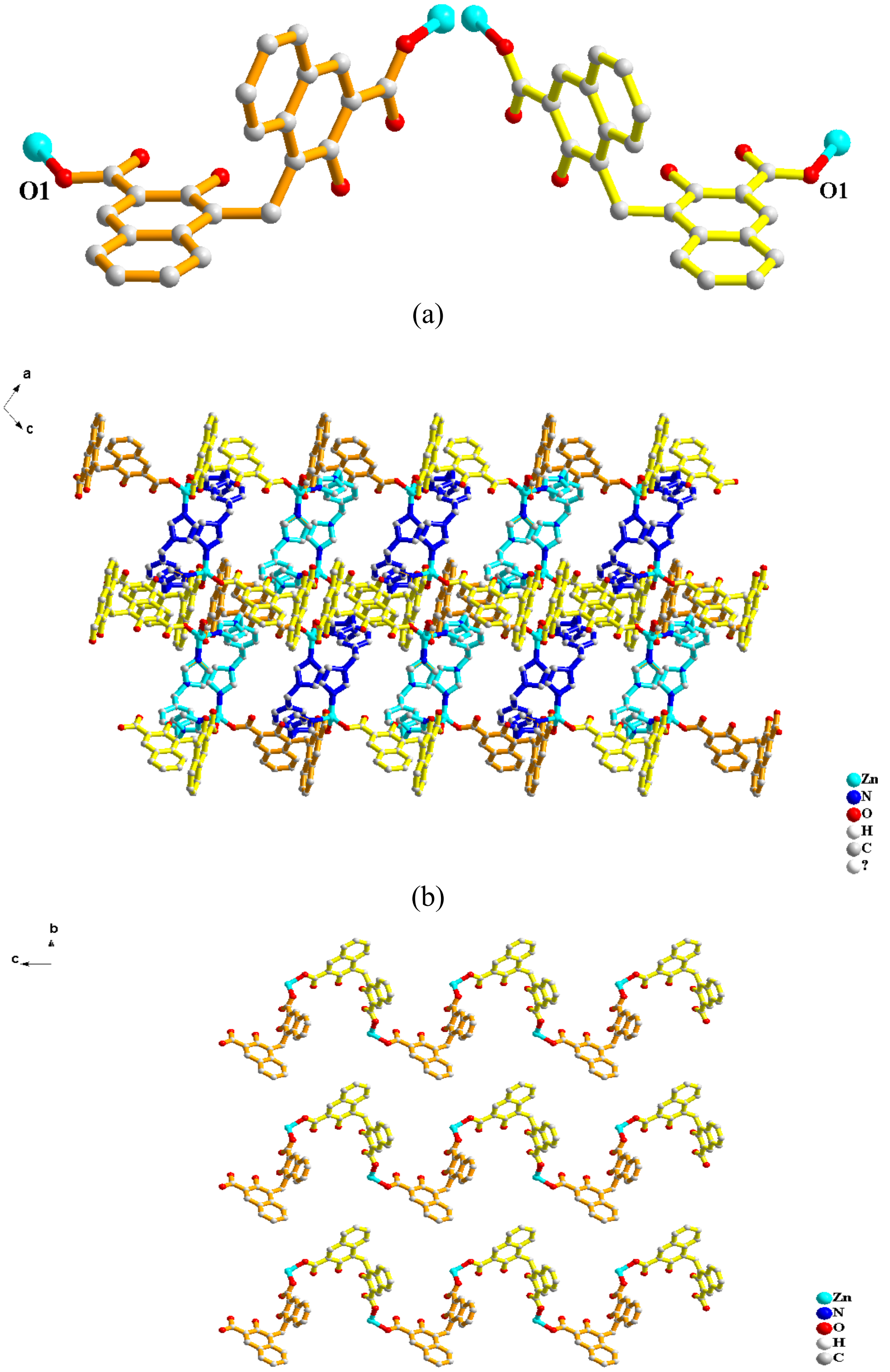


(a)

(b)

(c)

Fig. S2. View of the two glide-plane related conformation of the PA^{2-} ligand in ***β*** (a) and their arrangement in the three-dimensional supramolecular structure along *a* axis (b) as well as in the monolayer along *ac* plane (c), respectively. Two mirror-related conformations were in orange and yellow. In (c), bix ligands were omitted for clarity.



(a)

(b)

(c)

Fig. S3. View of the weak interactions between neighboring PA^{2-} and bix ligands from different layers of ***β***. Due to the overlap of the molecules, other parts were omitted for clarity. The C-H···π originates from the carbon hydrogen to naphthalene ring of PA^{2-} ligands. The C-H···O involves the methyl carbon hydrogen of DMF to the carboxylate oxygen atom as well as methylene carbon hydrogen of bix to DMF oxygen atom. The π···π stacking interactions were observed between the naphthalene ring of PA^{2-} ligands and benzene ring of bix ligands.

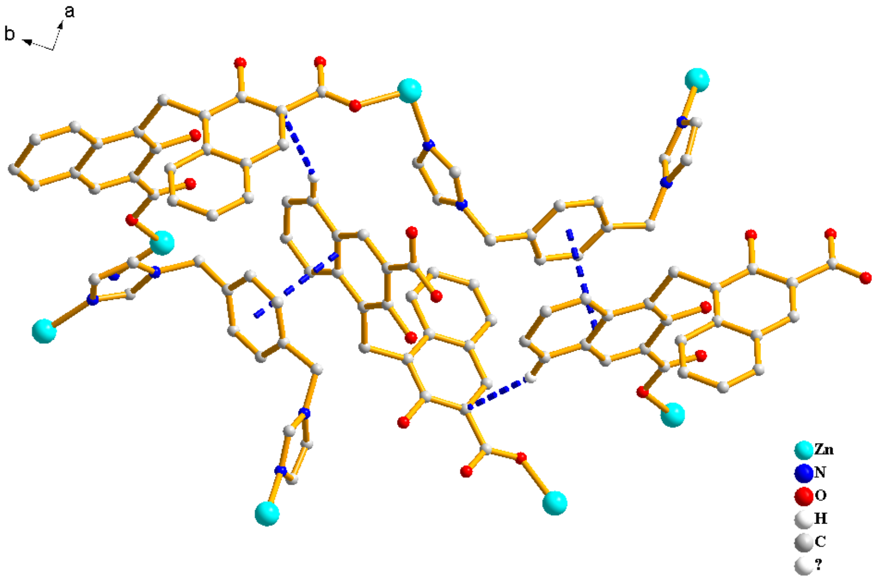


Fig. S4. 3-fold interpenetrating diamond structures of ***γ***.

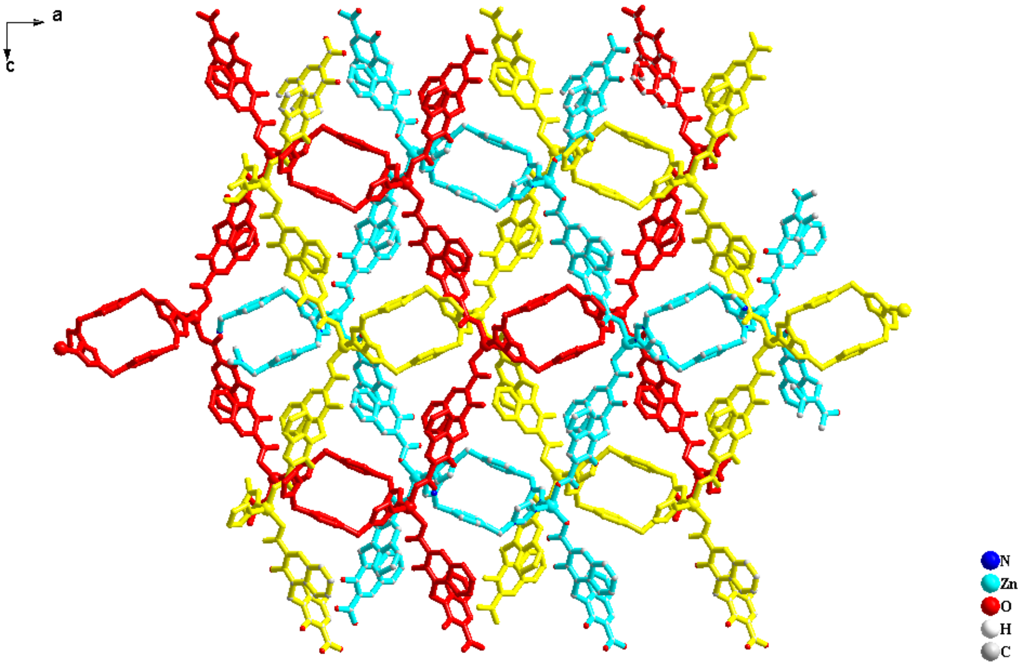


Fig. S5. Progression of ***α***-***γ*** from 2D simple layer and double layer to 3D framework, showing a trend from slightly distorted planar node toward tetrahedral node.

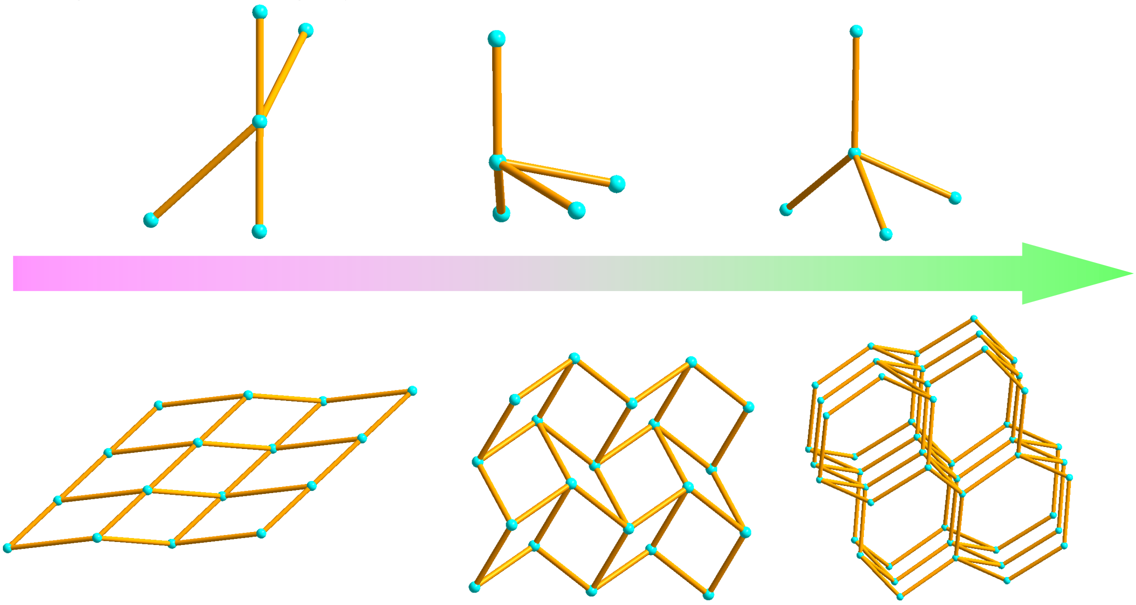
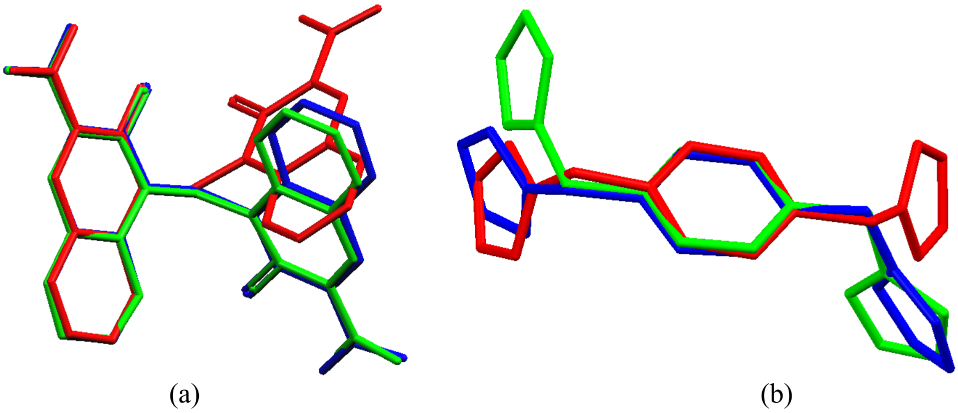


Fig. S6. Overlay of pamoate moieties (a) and bix ligands (b) of the three complexes. The red molecules of both PA and bix ligands exhibit *cis* conformations in ***β***. The blue and green molecules are all in *trans* conformations in ***α*** and ***γ***.



(a) (b)

Fig. S7. Powder XRD pattern of ***α***, (a) simulated and (b) as-synthesized.

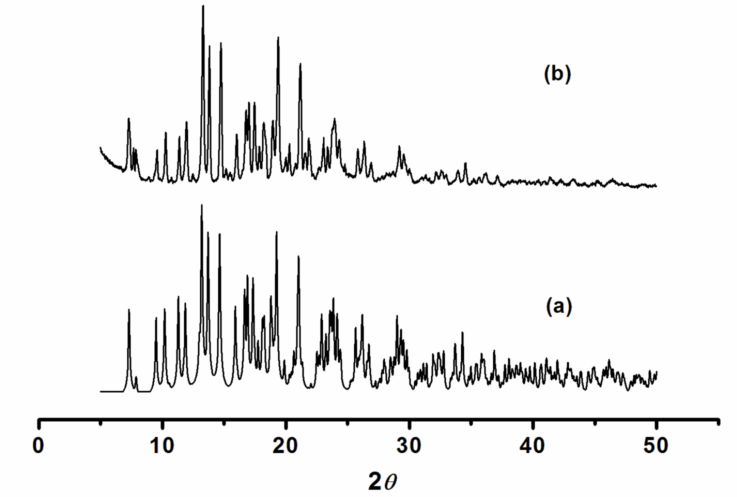


Fig. S8. Powder XRD pattern of ***β***, (a) simulated and (b) as-synthesized.

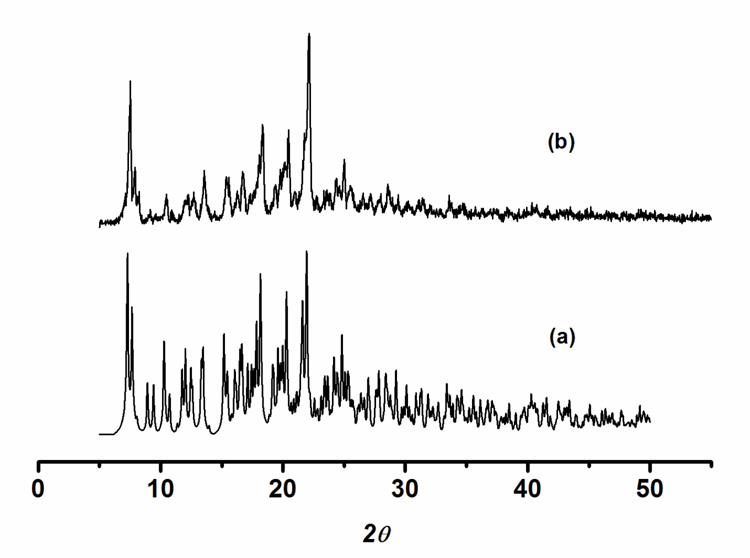


Fig. S9. (a) Powder XRD pattern of the simulated pure *γ*; (b) Powder XRD pattern of the unknown product obtained at 0ºC for several days in refrigerator; (c) Powder XRD pattern of the product obtained by heating the as-synthesized product at room temperature with DMF/CH_3OH in hydrothermal autoclave at 70ºC for 48h; (d) Powder XRD pattern of the original pure ***β***. This study indicates that the unknown phase at 0ºC converted completely to ***β*** through hydrothermal route. Thus, the unknown phase may be also a conformer of such supramolecular isomeric system. Due to the very poor crystalline of this product, attempts to obtain the single crystal for X-ray diffraction were unsuccessful.

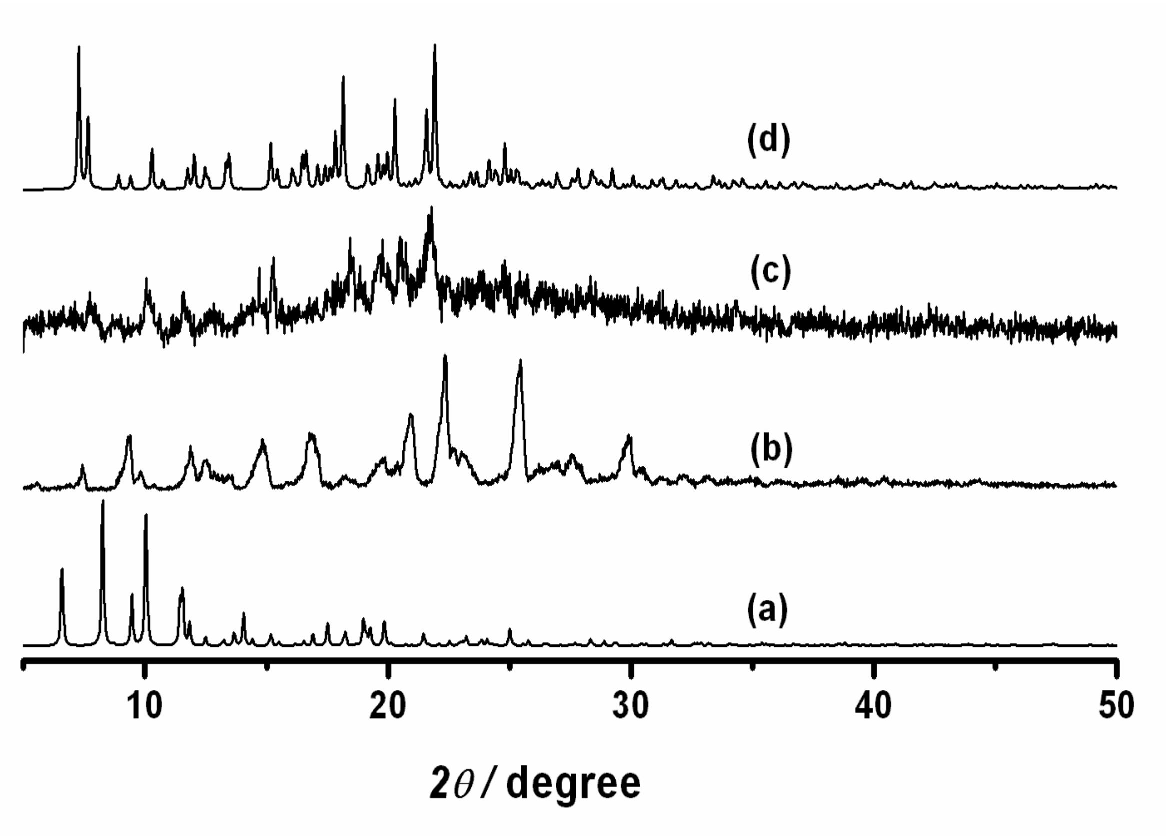


Fig. S10. (a) Powder XRD pattern of the simulated pure *γ*; (b) Powder XRD pattern of the product obtained at room temperature for several days with large amounts of *γ* and small amounts of ***β***; (c) Powder XRD pattern of the product obtained at 60ºC for 48h with large amounts of ***β*** and small amounts of *γ*; (d) Powder XRD pattern of the product obtained by heating the as-synthesized product at room temperature with DMF/CH_3OH in hydrothermal autoclave at 70ºC for 48h; (e) Powder XRD pattern of the product obtained by heating the as-synthesized product at room temperature with DMF/CH_3OH in hydrothermal autoclave at 100ºC for 48h; (f) (g) Powder XRD pattern of the original pure ***β***. This study indicates that *γ* converted completely to ***β*** through hydrothermal route.

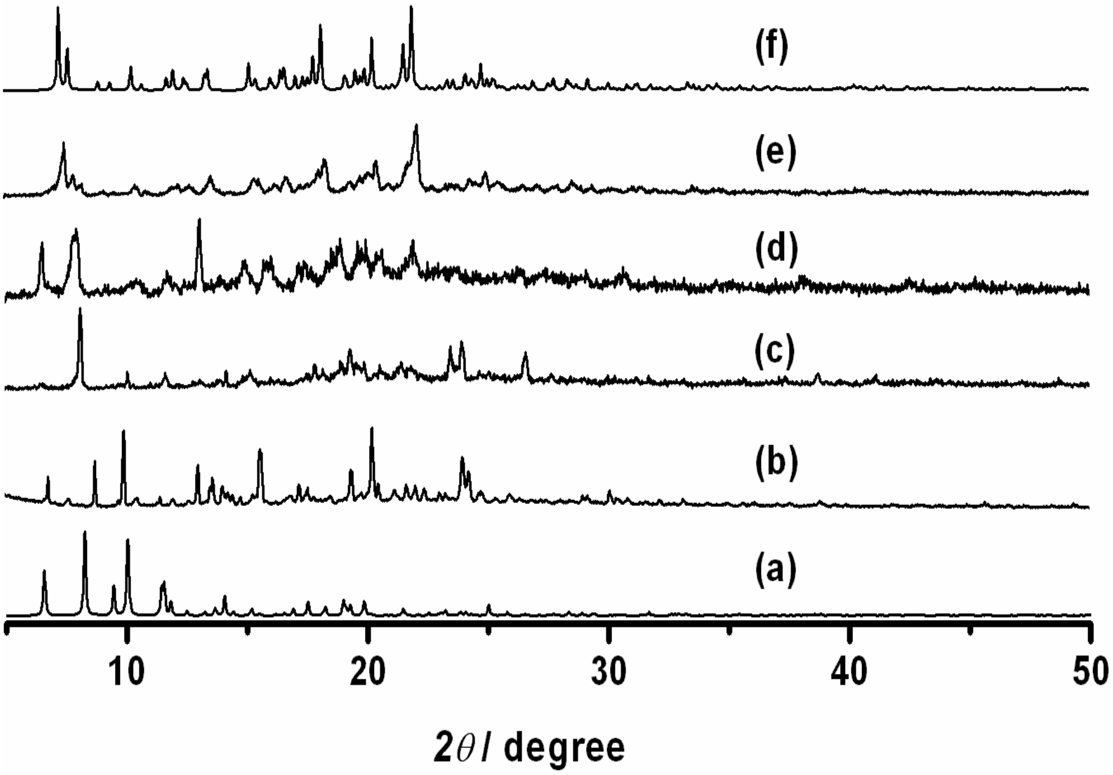


Fig. S11. (a)-(d) Powder XRD pattern of the pure ***β*** at 70, 90, 100 and 115 ºC for 48h, respectively; (e) Powder XRD pattern of the product obtained by heating the as-synthesized product at 100 ºC with DMF/CH_3OH in hydrothermal autoclave at 130ºC for 48h; (f) Powder XRD pattern of the original pure ***α***. This study indicates that ***β*** did not convert to ***α*** through the simple heating.

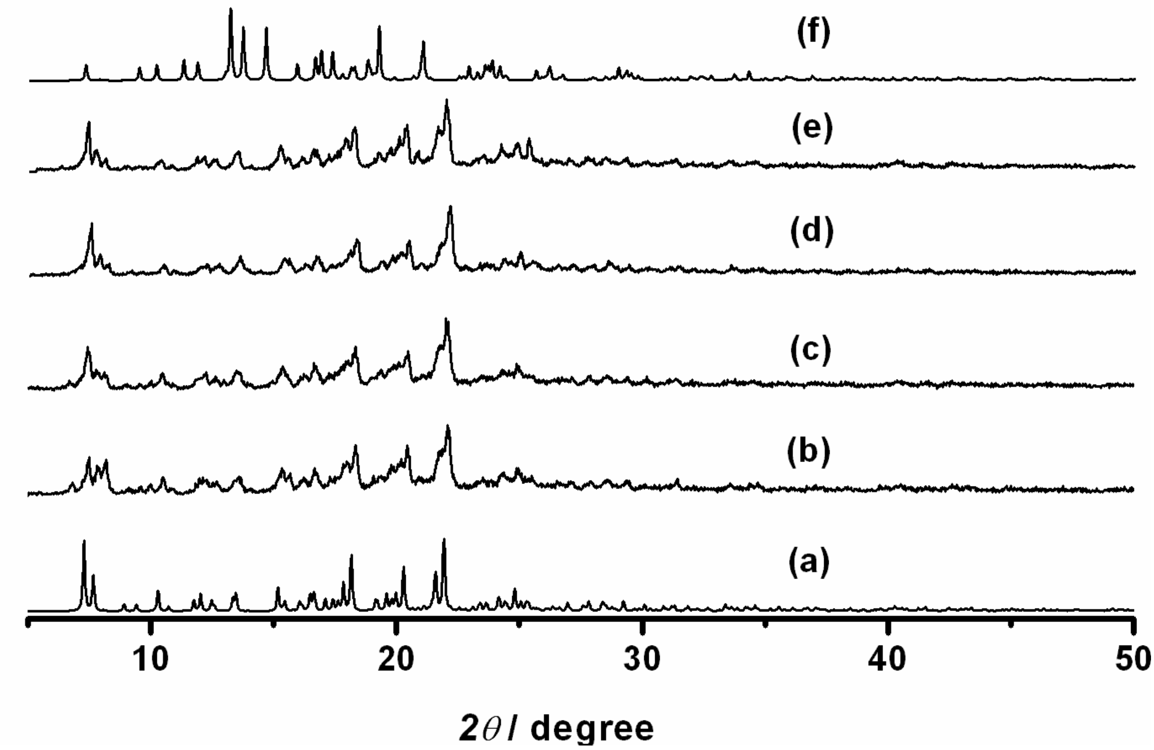


Fig. S12. Solid-state photoluminescence spectra of ***α*** (a) and ***β*** (b) at room temperature with the excitation at 420 nm.

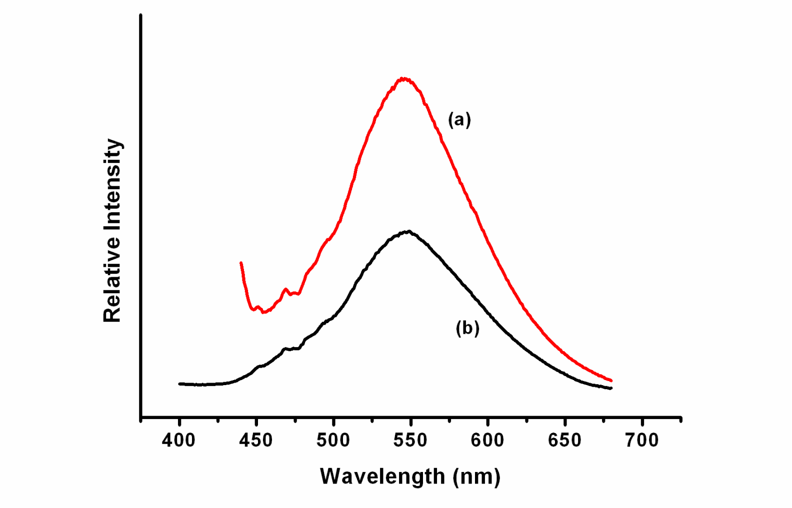


Fig. S13. TGA data of ***α*** and ***β***.