Supporting Information for

An unexpected helicity control and helix inversion: homochiral helical nanotubes consisting of an achiral ligand

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Experimental Section.

Materials and Methods. All starting chemicals were of reagent-grade quality and were obtained from commercial sources. All reagents and solvents were purified by standard methods. The FT-IR spectra were recorded in the region 400-4000 cm^{-1} on a Bruker EQUINOX 55 VECTOR22 spectrophotometer and the samples were prepared using KBr pellets. Elemental analyses were carried out with an Elmentar Vario EL-III analyzer. CD spectra were recorded on a Biologic MOS-450 CircularDichroism Spectrometer and the samples were prepared using KBr pellets. X-ray powder diffraction were recorded on a Bruker D8 Advance analyzer.

N,N,N´,N´-tetrakis(2-pyridyl)-2,6-pyridinediamine (tppda). The ligand tppda was synthesized by procedures reported earlier.[1]

A 2.565 g (15 mmol) sample of 2,2′-dipyridylamine,1.185 g (5 mmol) of 2,6-dibromo-pyridine, 3.45 g (25 mmol)of anhydrous potassium carbonate, and 0.19 g (0.76 mmol) of cupric sulfate pentahydrate were placed in a 50 ml flask. The mixture was heated to 220 ℃ and stirred for 8h under N_2. The reaction was monitored by TLC. After the reaction mixture was cooled to ambient temperature, dichloromethane and water were added to dissolve the solids. The aqueous phase was discarded, and the organic phase was washed with distilled water to neutral pH and then dried with $MgSO_4$. The product was isolated by using a chromatographic column with ethyl acetate as the eluent to obtain the colorless solid of N,N,N′,N′-tetra(2-pyridyl)-2,6-pyridinediamine (**tppda**) (1.36g, 65%). ^{1}H-NMR (300 MHz; $CDCl_3$; 300K; δ, ppm): 8.30 (d, 4H), 7.50 (t, 5H), 7.07 (d, 4H), 6.95 (t, 4H), 6.68 (d, 2H).

1,3-Bis(di-2-pyridyamino)benzene (bpab). A 2.565 g (15 mmol) sample of 2,2′-dipyridylamine, 1.180 g (5 mmol) of 1,3-dibromobenzene, 3.45 g (25 mmol) of anhydrous potassium carbonate, and 0.25 g (1 mmol) of cupric sulfate pentahydrate were placed in a 50 ml flask. The mixture was heated to 200~220 ℃ and stirred for 9h under N_2. The reaction was monitored by TLC. After the reaction mixture was cooled to ambient temperature, dichloromethane and water were added to dissolve the solids. The aqueous phase was discarded, and the organic phase was washed with distilled water to neutral pH and then dried with $MgSO_4$. The product was isolated by using a chromatographic column with ethyl acetate as the eluent to obtain the colorless solid of 1,3-bis(di-2- pyridyamino)benzene (**bpab**) (1.27g, 61%). ^{1}H-NMR (300 MHz; $CDCl_3$; 300K; δ, ppm): 8.52 (m, 4H), 7.70 (m, 4H), 7.03~7.21 (m, 11H).

3,5-Bis(di-2-pyridyamino)pyridine (bpap). A 2.565 g (15 mmol) sample of 2,2′-dipyridyl -amine,1.185 g (5 mmol) of 3,5-dibromopyridine, 3.45 g (25 mmol) of anhydrous potassium carbonate, and 0.25 g (1 mmol) of cupric sulfate pentahydrate were placed in a 50 ml flask. The mixture was heated to 200~220 ℃ and stirred for 9h under N_2. The reaction was monitored by TLC. After the reaction mixture was cooled to ambient temperature, dichloromethane and water were added to dissolve the solids. The aqueous phase was discarded, and the organic phase was washed with distilled water to neutral pH and then dried with $MgSO_4$. The product was isolated by using a chromatographic column with ethyl acetate as the eluent to obtain the colorless solid of 3,5-bis(di-2- pyridyamino)pyridine (**bpap**) (1.33g, 64%). ^{1}H-NMR (300 MHz; $CDCl_3$; 300K; δ, ppm): 8.40 (d, 4H), 8.12 (s, 2H), 7.72~7.80 (m, 5H), 7.10~7.17 (m, 8H).

1,3-Bis(di-2-pyridyamino)-5-fluorobenzene (bpafb). A 2.565 g (15 mmol) sample of 2,2′-dipyridylamine,1.270 g (5 mmol) of 1,3-dibromo-5-fluorobenzene, 3.45 g (25 mmol) of anhydrous potassium carbonate, and 0.25 g (1 mmol) of cupric sulfate pentahydrate were placed in a 50 ml flask. The mixture was heated to 200~220 ℃ and stirred for 9h under N_2. The reaction was monitored by TLC. After the reaction mixture was cooled to ambient temperature, dichloromethane and water were added to dissolve the solids. The aqueous phase was discarded, and the organic phase was washed with distilled water to neutral pH and then dried with $MgSO_4$. The product was isolated by using a chromatographic column with ethyl acetate as the eluent to obtain the colorless solid of 1,3-bis(di-2-pyridyamino)-5- fluorobenzene (**bpafb**) (1.31g, 60%). ^{1}H-NMR (300 MHz; $CDCl_3$; 300K; δ, ppm): 8.337~8.317 (q, 4H), 7.615~7.563 (q, 5H), 7.098~7.071 (d, 4H), 6.990~6.949 (q, 4H), 6.750 (s, 1H), 6.696~6.621 (q, 2H).

Synthesis of $[Cd(tppda)(NO_3)_2]_n\cdot nDMF$ (1-*P*-a). 30 ml methanol solution of the tppda (0.0417 g, 0.1 mmol) was slowly added to a 20 ml methanol solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.0308 g, 0.1 mmol). The mixture was stirred at room temperature for 4 h in a 100 ml flask. The resulting solution was concentrated *in vacuo* and the solid product was slowly added to a 3 ml DMF. The solution was filtered and the resulting mixture was left in the dark for slow diffusion of ether vapor. Yellowish octahedral crystals of **1-*P*-a** suitable for X-ray structure analysis were obtained after several weeks. Yield: 0.0378 g, 52%. Anal. Calcd. for $C_{28}H_{26}CdN_{10}O_7$: C, 46.26; H, 3.605; N, 19.27. Found: C, 46.25; H, 3.590; N, 19.36. IR (cm^{-1}): 3434(s), 3076(m), 1672 (vs, CO for DMF), 1603(vs), 1566(vs), 1467(s), 1428(vs), 1385(s, for NO_3^-), 1308(s), 1152(m), 775(m), 758(m).

Synthesis of $[Cd(tppda)(NO_3)_2]_n \cdot 0.5nMeOH$ (1-*P*-b). 1-*P*-b was prepared using the same method as for **1-*P*-a**. In the final reaction step, a 3 ml N, N-dimethylacetamide (DMAC) solution was added instead of DMF for **1-*P*-a** preparation. The solution was filtered and the resulting mixture was left in the dark for slow diffusion of ether vapor. Yellowish octahedral crystals of **1-*P*-b** suitable for X-ray structure analysis were obtained several weeks later. Yield: 0.0226 g, 34%. Anal. Calcd. for $C_{25.5}H_{21}CdN_9O_{6.5}$: C, 45.72; H, 3.160; N, 18.82. Found: C, 45.67; H, 3.261; N, 18.76. IR (cm^{-1}): 3435(s), 1602(vs), 1566(vs), 1467(s), 1428(vs), 1384(s, for NO_3^-), 1309(s), 1155(m), 775(m), 757(m).

The solvothermal method: A mixture of of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0924 g, 0.3 mmol), the tppda (0.0417 g, 0.1 mmol) and 4 ml MeOH was sealed in a ~ 5-mL glass tube, heated at 120-140 °C for 3 days, and slowly cooled to room temperature. Yellowish polyhedral crystals of ***1-P-b*** were obtained. Yield: 0.0539g. (The single-crystal X-ray diffraction study revealed that the crystallographic parameters of ***solvothermal*** crystals are similar to those of ***1-P-b***.)

Synthesis of Cd^{II} complex 1-*P*-c. 1-*P*-c was prepared using the same method as for **1-*P*-a**, except for not adding DMF in the final reaction step. Yellowish octahedral crystals of **1-*P*-c** were obtained several days later. However, this complex is too air-sensitive and very unstable at room temperature and low temperature. The X-ray data collection for structure analysis was failed. Yield: 0.0459 g.

Synthesis of $[Cd(tppda)(NO_3)_2]_n \cdot nSolvent$ (1-*M*). A mixture of of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0924 g, 0.3 mmol), the tppda (0.0417 g, 0.1 mmol) and 4 ml H_2O was sealed in a ~ 5-mL glass tube, heated at 120-140 °C for 3 days, and slowly cooled to room temperature. Yellowish polyhedral crystals of **1-*M*** were obtained. Yield: 0.0512 g. IR (cm^{-1}): 3423(m), 1602(vs), 1565(s), 1467(s), 1427(vs), 1384(s, for NO_3^-), 1308(s), 1154(m), 774(m), 757(m).

X-ray Crystallography. Data collections for all compounds were performed with Mo Ka radiation (λ = 0.71073 Ǻ) on a Bruker SMART Apex CCD diffractometer. Absorption corrections were applied by using multi-scan program SADABS.[2] All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with SHELXTL.[3] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on organic ligands of all compounds were generated by riding mode (C–H 0.93 Ǻ). Crystallographic data for all compounds are summarized in Tables S1.

Table S1. Crystallographic data for the ligands and the complexs.

	1-*P*-a	**1-*P*-b**	**bpab·3H$_2$O**	**bpafb**
CCDC	712882	712881	712884	712885
formula	$C_{28}H_{26}CdN_{10}O_7$	$C_{25.5}H_{21}CdN_9O_{6.5}$	$C_{26}H_{26}N_6O_3$	$C_{26}H_{19}FN_6$
Formula weight	726.99	669.91	470.53	434.47
T/K	173(2)	293(2)	293(2)	293(2)
λ(Mo-K$_\alpha$) Å	0.71073	0.71073	0.71073	0.71073
crystal system	hexagonal	hexagonal	monoclinic	monoclinic
crystal size/mm^3	0.35*0.32*0.28	0.15*0.14*0.14	0.32*0.30*0.25	0.41*0.15*0.15
space group	P6(1)22	P6(1)22	P2(1)/c	P2(1)/c
a/Å	15.7763(4)	16.0598(6)	15.439(3)	13.9282(18)
b/Å	15.7763(4)	16.0598(6)	8.1148(18)	16.957(2)
c/Å	20.7324(8)	21.0558(15)	20.524(5)	9.4902(12)
α/deg	90.00	90.00	90.00	90.00
ß /deg	90.00	90.00	110.613(5)	105.412(2)
γ /deg	120.00	120.00	90.00	90.00
V/Å^3	4468.8(2)	4703.1(4)	2406.8(9)	2160.8(5)
Dc/Mg m^{-3}	1.621	1.419	1.299	1.336
Z	6	6	4	4
F(000)	2208	2022	992	904
μ/mm^{-1}	0.798	0.749	0.088	0.089
reflections collected	84653	24719	8075	10729
reflections unique	3711	2773	4092	3786
R$_{int}$	0.0682	0.0671	0.0429	0.0334
data/restraints/params	3711 / 0 / 232	2773 / 1 / 197	4092 / 0 / 316	3786 / 0 / 299
Final R indices[$I>2\sigma(I)$]	$R_1 = 0.0364$ $wR_2 = 0.0915$	$R_1 = 0.0705$ $wR_2 = 0.2073$	$R_1 = 0.0810$ $wR_2 = 0.2037$	$R_1 = 0.0511$ $wR_2 = 0.1397$
R indices(all data)	$R_1 = 0.0418$	$R_1 = 0.1056$	$R_1 = 0.1555$	$R_1 = 0.0743$

	wR_2 = 0.0997	wR_2 = 0.1742	wR_2 = 0.2556	wR_2 = 0.1664
GOF on F^{2-}	1.188	1.150	1.069	1.033

Crystal describe Section.

(1) Crystal structure of [Cd(tppda)$(NO_3)_2$]$_n$·nDMF (1-*P*-a)

Yellowish octahedral crystals of [Cd(tppda)$(NO_3)_2$]$_n$·nDMF (**1-*P*-a**) were obtained from DMF/MeOH solution containing tppda and $Cd(NO_3)_2 \cdot 4H_2O$ in a 1:1 molar ratio by slow diffusion of ether vapour. A single-crystal X-ray diffraction study revealed that **1-*P*-a** crystallizes in the chiral hexagonal space group P6(1)22 and consists of a chiral neutral framework. Each Cd^{2+} ion is coordinated by two oxygen atoms from a pair of NO_3^- anions (Cd–O 2.351(3) Å) and four bridging nitrogen atoms from two dpa groups of different tppda ligands (Cd–N 2.282(3) and 2.393(8) Å) to form a distorted octahedral geometry. Crystallographically equivalent Cd^{II} ions are bridged by tppda spacers to form an infinite helical chain along the c axis. The right-handed helix is generated around the crystallographic 6(1) axis with a helical pitch of 20.73 Å, which is the *c*-axis length. A detailed inspection of **1-*P*-a** reveals that the helix structure is stabilized by alternating π···π stacking interactions of pyridyl groups from ligands (centroid to centroid separations of 3.74 Å). Additionally, π···π stacking interactions are established via pyridyl groups of tppda belonging to neighbor helices (centroid to centroid separations of 3.56 Å). Each helix encases with the other six helices to give a periodically ordered architecture. The helices inlay one another to form a 3D chiral framework with 1D open channels. The distance of the nearest carbon atom to the helical axis of the nanotube is ca. 3.59 Å, while the distance of the farthest carbon atom is ca. 10.66 Å, which implies a thick-wall nanotube (~7 Å). Calculations using PLATON show that the cavity in the 1D channel has an effective volume for inclusion of 917.8 $Å^3$ per helical turn. This cavity is nearly fully filled by the DMF guest molecules (836.7 $Å^3$), which occupy 18.7% of the crystal volume.

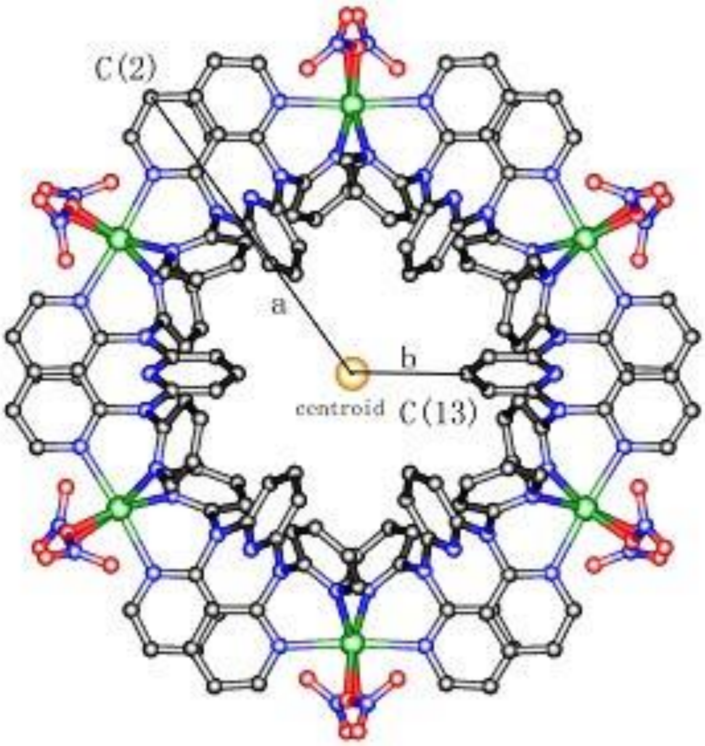

Figure S1. Top view of complexes **1-*P*-a** and **1-*P*-b,** showing the thickness of wall in the nanotube. (**1-*P*-a :** a = 10.6629 (3) Å and b = 3.5949 (1) Å; **1-*P*-b :** a = 10.7562 (2) Å and b = 3.8150 (1) Å). Blue, N; gray, C; green, Cd; red, O. Hydrogen atoms were omitted for clarity.

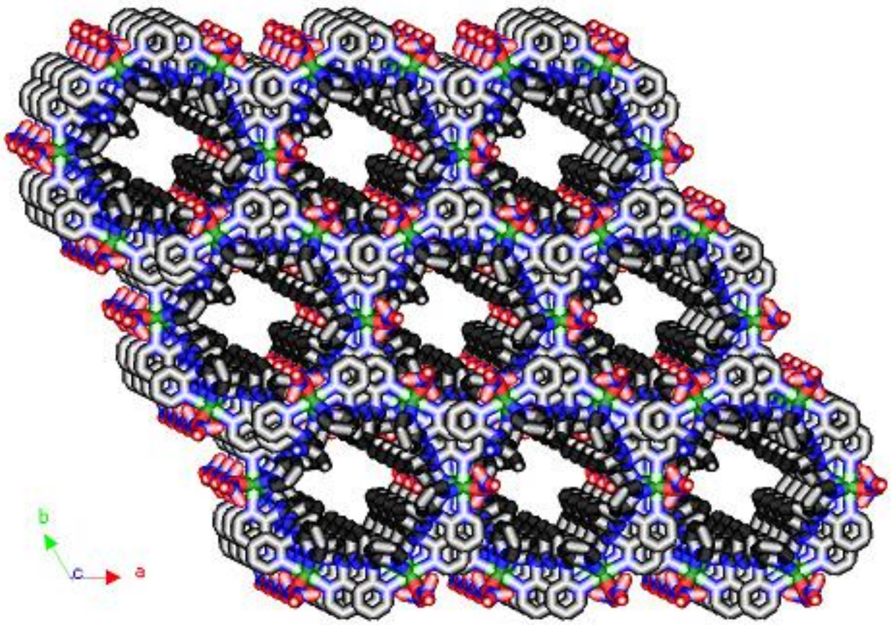

Figure S2. The 3D nanotubular framework of ***1-P-a*** and ***1-P-b*** viewed along c-axis. (H atoms and guest molecules omitted for clarity.)

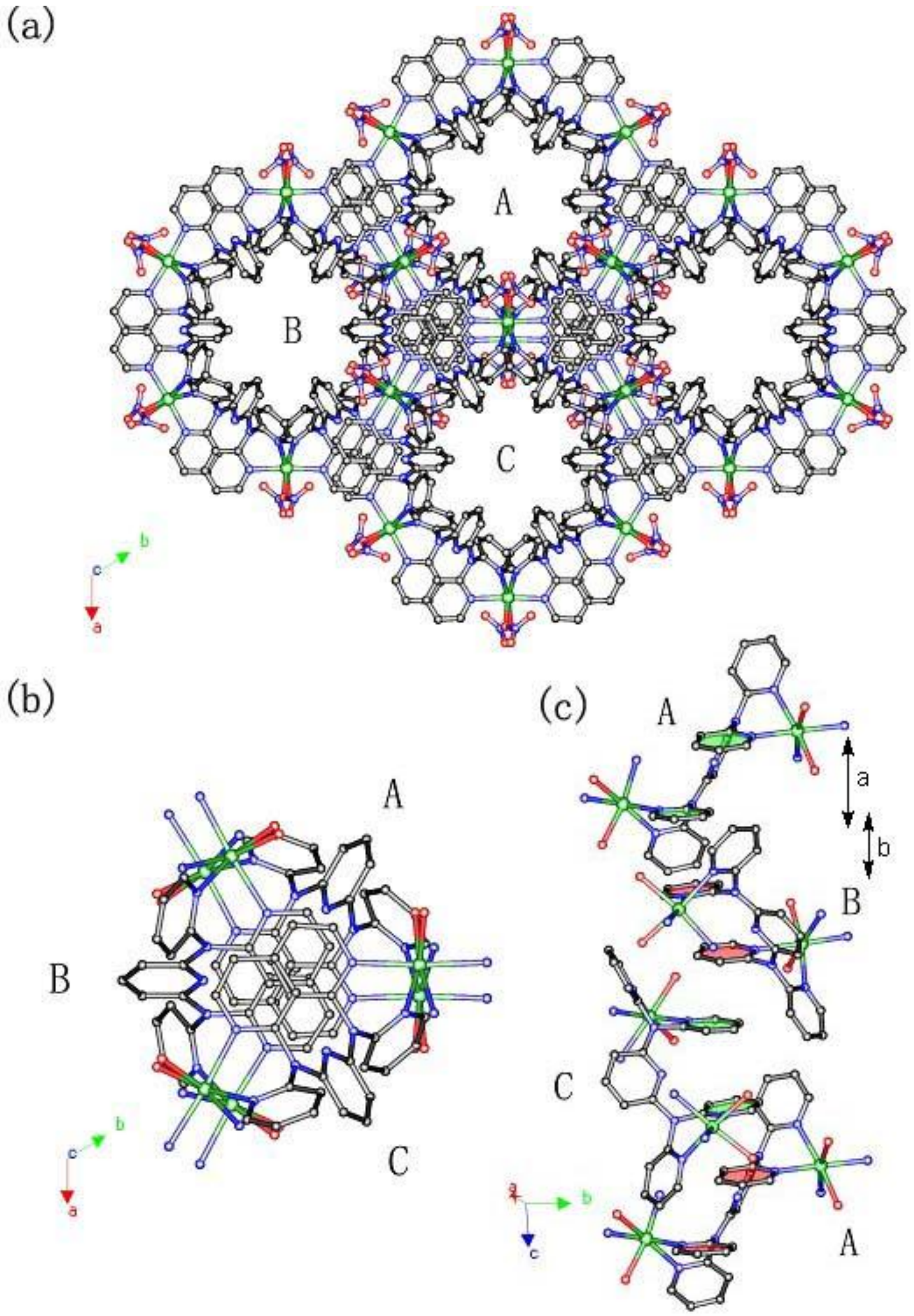

Figure S3. 3D network viewed along *ab* plane in compounds **1-*P*-a** and **1-*P*-b**, showing the face-to-face $\pi\cdots\pi$ stacking interactions between helix chains (Complexe **1-*P*-a :** $d_{centroid\text{-}centroid}$ a = 4.1200(1)Å, b = 3.5564(1)Å and dihedral angle a = 8.40° , b = 6.01° ; Complexe **1-*P*-b :** $d_{centroid\text{-}centroid}$ a = 4.2061(1) Å, b = 3.65428 (9) Å and dihedral angle a = 7.10° , b = 6.53°). Blue, N; gray, C; green, Cd; red, O. Hydrogen atoms have been omitted for clarity.

(2) Crystal structure of [Cd(tppda)(NO_3)$_2$]$_n$·0.5nMeOH (1-*P*-b)

With the success of incorporating DMF as the guest molecule in the 1D helical architecture, we attempted to assemble the helical structure with a larger channel and different helical pitch by using a bigger guest template, N,N-dimethylacetamide (DMA). However, employing the same procedure as in the case of DMF, introduction of DMA into the nanotube was not achieved. Instead methanol molecules from the solvent mixture were incorporated and [Cd(tppda)(NO_3)$_2$]$_n$·0.5nMeOH (**1-*P*-b**) was formed. This is probably due to the limited spaces of the channels and the preference of a six-fold helix in the Cd^{II}-tppda coordination.

1-*P*-b adopts a tubular architecture almost identical to that of **1-*P*-a**. The right-handed helix consists of alternating Cd(NO_3)$_2$ and tppda around the 6_1 axis with a pitch of 21.06 Å, which form a chiral nanotube with an opening similar to **1-*P*-a**. The helix and framework structures of **1-*P*-b** is, as in **1-*P*-a**, stabilized by two types of face-to-face π-stacking interactions between pyridyl groups. The centroid to centroid separations are 3.86 Å for the intramolecular stacking and 3.65 Å for the intermolecular one. The effective volume for inclusion is 1013.8 Å^3 in the 1D channels, comprising 21.6% of the crystal volume.

The crystallization of a cadmium complex was also carried out by using the methanol-ether diffusion procedure without adding DMF to the solution. An octahedral crystal **1-*P*-c** was obtained, however, it was too air-sensitive for the crystallographic measurements even at low temperature. The appearance and the data from IR, PXRD and crystal patterns show **1-*P*-c** is similar to **1-*P*-a** and **1-*P*-b**, implying the same type of helical structure.

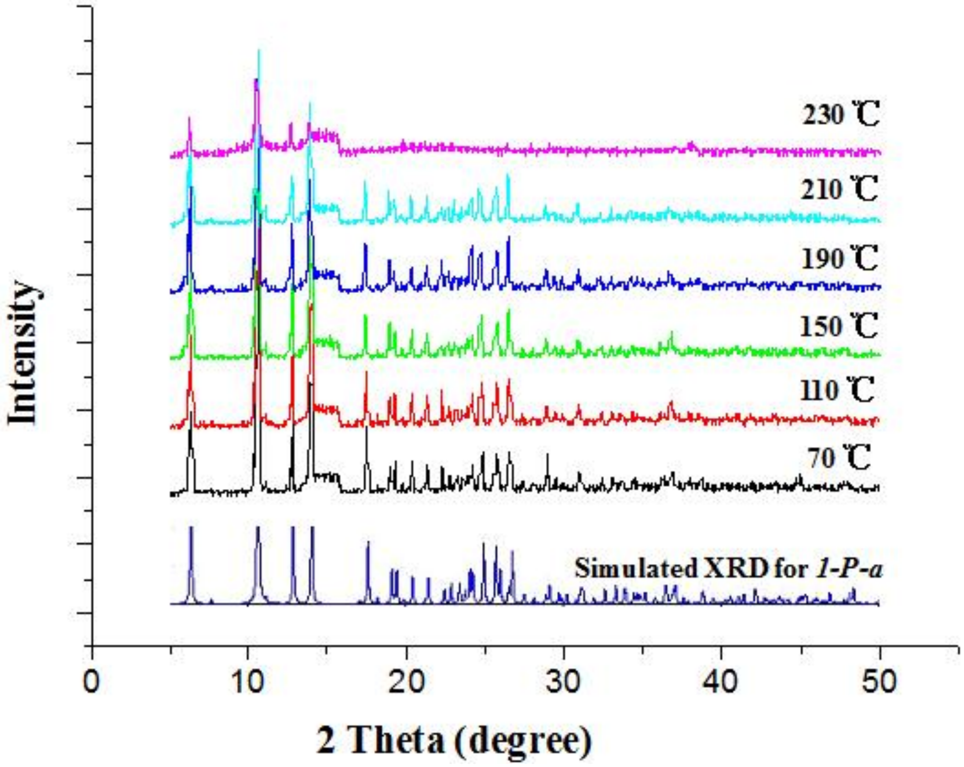

Figure S4. X-ray powder diffraction of **1-*P*-a** heated at various temperatures. Results show that the complex **1-*P*-a** is stable up to 210℃.

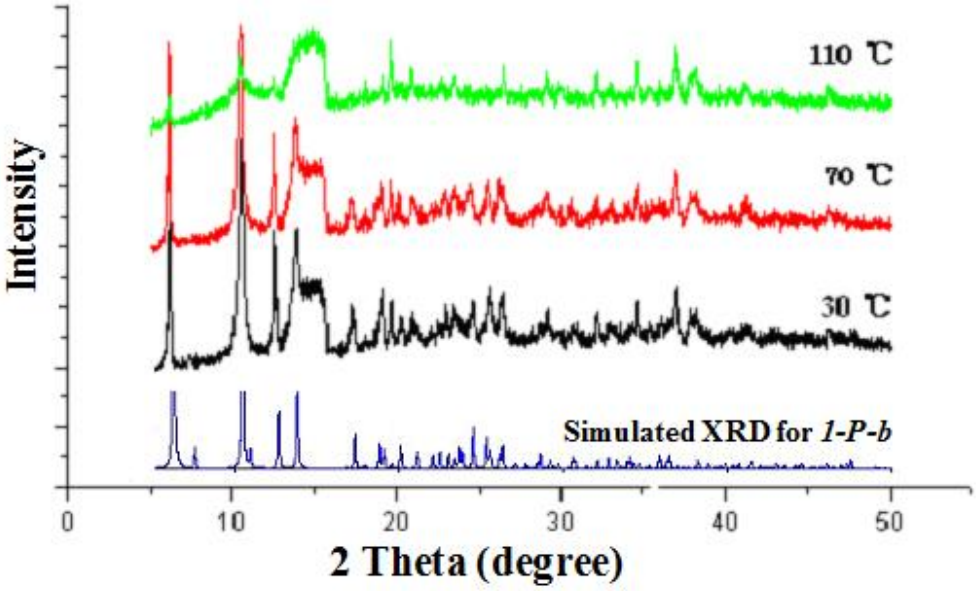

Figure S5. X-Ray powder diffraction of **1-*P*-b** heated at various temperatures. Results show that the complex **1-*P*-b** is stable up to 70℃.

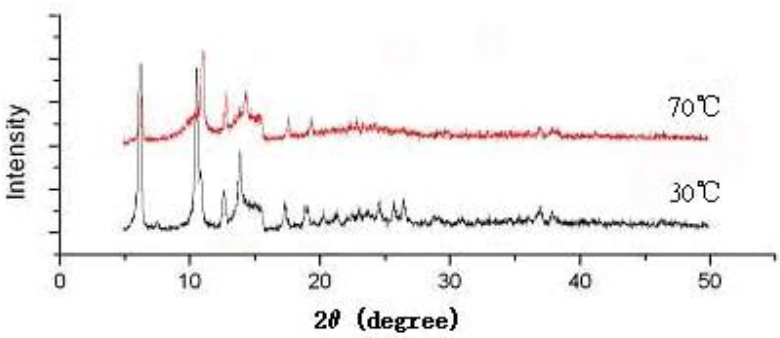

Figure S6. X-Ray powder diffraction plots of **1-*P*-c** shows that complex **1-*P*-c** is stable less than 30℃.

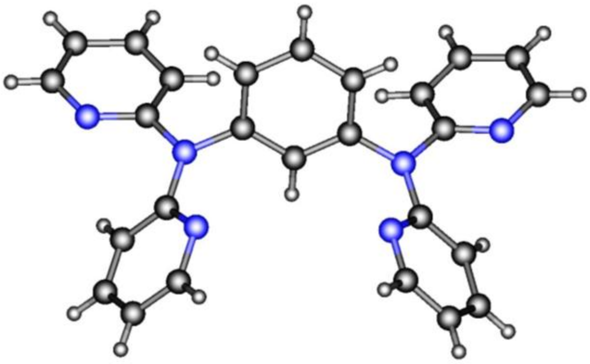

Figure S7. Single-crystal X-ray structure of the **bpab**.

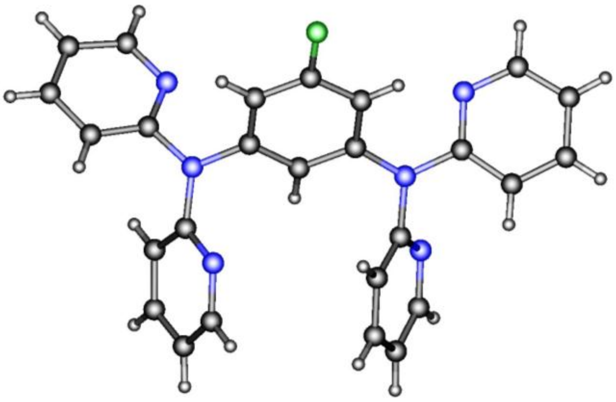

Figure S8. Single-crystal X-ray structure of the **bpafb**.

References

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[3] G. M. Sheldrick, SHELXTL, Version 6.10, Siemens Industrial Automation Inc., Madison, Wisconsin, USA, **2000**.