

Supporting Information

Ligand-conformation driving chiral generation and symmetry-breaking crystallization of a zinc(II) organoarsenate

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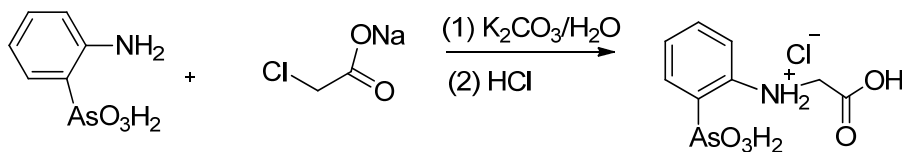
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Materials and Methods.

2-Aminobenzenearsonic acid (98%) was obtained from TCI (Tokyo, Japan) and used as received. Chloroacetic acid sodium salt (98%) was purchase from J&K Chemical Ltd (China). All of the other chemical were obtained from sinopharm chemical Reagent Co. Ltd (China) and used without further purification. Elemental analyses (C, H, N) were performed on a German Elementary Vario El III instrument. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000–400 cm⁻¹. Thermogravimetric analyses (TGA) were carried out with a NETZSCH STA 449C unit at a heating rate of 15 °C/min under an air atmosphere. Powder X-ray diffraction (XRD) patterns were collected on an XPERT-MPD θ -2 θ diffractometer. Photoluminescence analyses were performed on a Perkin Elemer LS55 fluorescence spectrometer. The measurement of the powder frequency-doubling effect was carried out on the sieved (80–100 mesh) powder sample of compound 2 by means of the modified method of Kurtz and Perry.¹ The fundamental wavelength is 1064 nm generated by a Q-switched Nd: YAG laser. Sieved KDP powder (80–100 mesh) was used as a reference. The solid-state CD spectra was carried out with a MOS-450 spectropolarimeter using a mixture of about 0.7-1.3 mg sample and 35-65 mg dried KCl powder, which was well grounded and then pressed into a disk for use in the CD measurement.

X-ray Crystallography: Data collections were performed on performed on a Rigaku SCXMini CCD diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. All data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan method. All structures were solved by the direct methods and refined by full-matrix least-squares fitting on

F^2 by SHELX-97.



Scheme 1. Preparation of ligand H₃capa

Synthesis of 2-(carboxymethylamino)phenylarsonic acid (H₃capa-HCl).

2-Aminobenzenearsonic acid (43.6 g, 0.2mol) was dissolved in a solution of K₂CO₃ (g, 0.5mol) in water. To the resulting mixture, chloroacetic acid sodium salt (29.3g, 0.25) was added in portions with gentle stirring and the mixture was refluxed 7 h at 100 °C. Then the reaction mixture was cooled to room temperature, and then acidified with concentrated HCl to a pH value of 2.0–2.5. The resulting precipitate was filtered off, washed with cold water. The crude product was purified by recrystallization from H₂O, and then dried under reduce pressure to give H₃capa-HCl in 60% yield (33 g). ¹H NMR (400 MHz, D₂O): 3.91 (s, 2H), 6.65 (d, 1H, *J* = 8.8 Hz), 6.82 (t, 1H, *J* = 7.6 Hz), 7.42 (t, 1H, *J* = 7.2 Hz), 7.48 (d, 1H, *J* = 6.4 Hz). Calcd for C₈H₁₁AsClNO₅: C, 30.84; H, 3.56; N, 4.50. Found: C, 30.79; H, 3.41; N, 4.48.

Synthesis of Zn(Hcapa)(4, 4'-bipy) (1P or 1M).

A mixture of Zn(NO₃)₂·6H₂O (0.133 g, 0.45 mmol), H₃capa (0.031 g, 0.1 mmol) and 4, 4'-Bipy (0.067 g, 0.4 mmol) and H₂O (6 mL), followed by addition of four drops of (CH₃)₄NOH, was stirred and kept in a Scintillation Vial at 85 °C for 48 hrs. After cooling to room temperature, the yellow block single crystals of compound 2 were filtered off, washed with distilled water, and dried in air. The initial and final pH values of the solution were 7.0 and 6.5, respectively. Yield: 65% (0.032 g) based on H₃capa. Anal. Calcd for C₁₈H₁₆AsN₃O₅Zn: C, 43.70; H, 3.26; N, 8.49. Found: C, 43.52; H, 3.28; N, 8.56. IR (KBr, cm⁻¹): 3346 (m), 3063 (w), 3008 (w), 2920 (s), 2852 (w), 1593 (br), 1521 (w), 1484 (w), 1458 (m), 1430 (w), 1410 (w), 1390 (br), 1258 (w), 1217 (m), 1200 (w), 1157 (m), 1132 (w), 1101 (w), 1065 (w), 1045 (m), 1019 (w), 1007 (w), 961 (w), 900 (s), 867 (s), 808 (s), 772 (s), 742 (s), 728 (w), 675 (w), 626 (s), 574 (m).

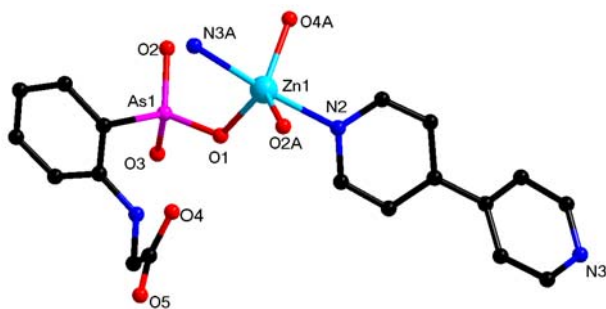
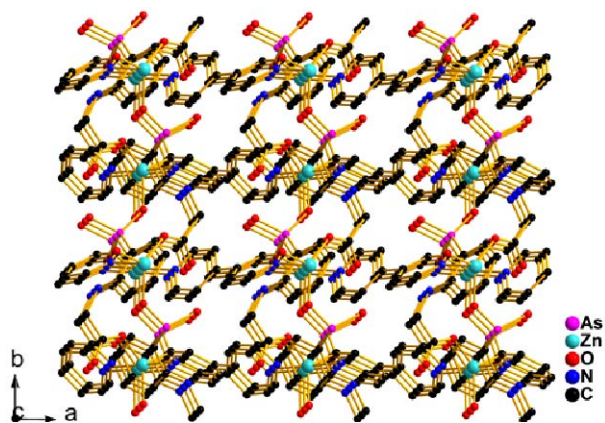
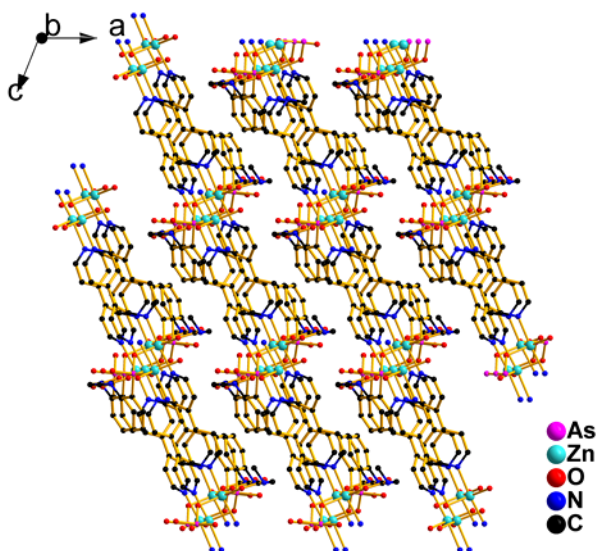


Fig. S1 View of an asymmetric unit in compound **1P**. Symmetry transformations used to generate equivalent atoms: (A) $-x, y-1/2, -z-1$ for O2A, $-x, y+1/2, -z-1$ for O4A, $x-1, y, z-1$ for N3A.



(a)



(b)

Fig. S2 View of the structure of compound **1P** down the *c*-axis (a), and along the *b*-axis (b).

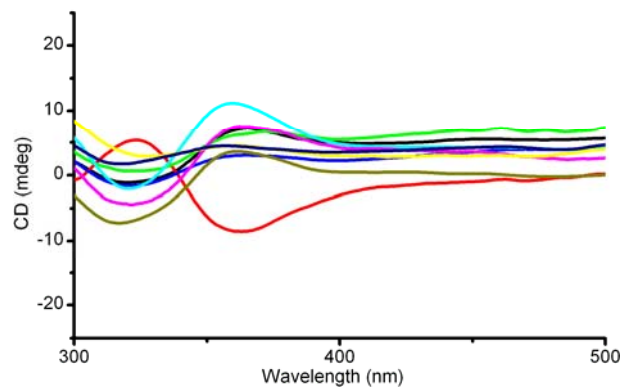


Fig. S3 Solid-state CD spectra of samples of compound **1P** and **1M**

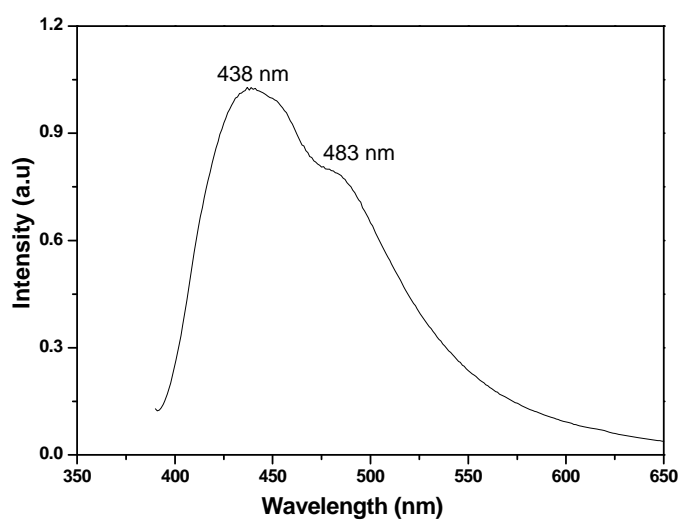


Fig. S4. The luminescence spectrum of the ligand H₃capa excited at 378 nm at room temperature.

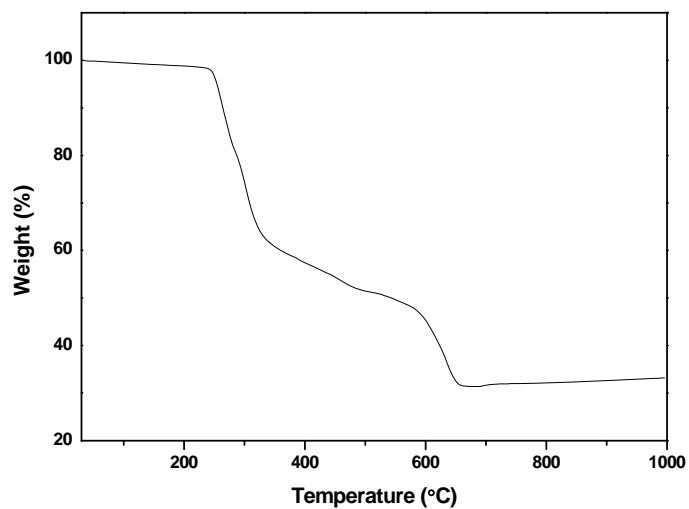


Fig. S5. The TGA diagram of **1P** or **1M**.

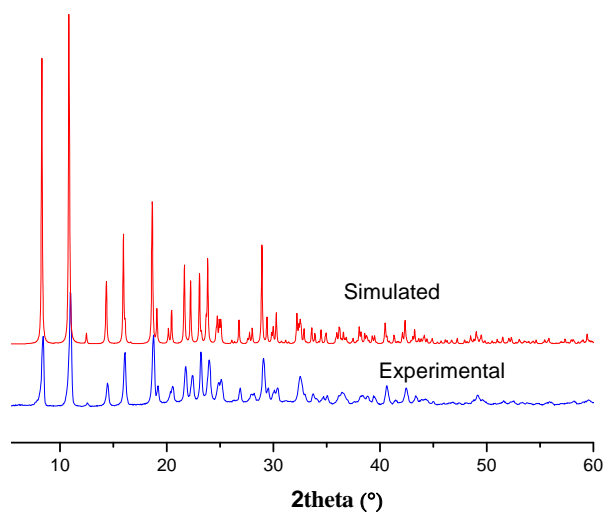


Fig S6. Simulated and experimental XRD powder patterns for compound **1P** or **1M**

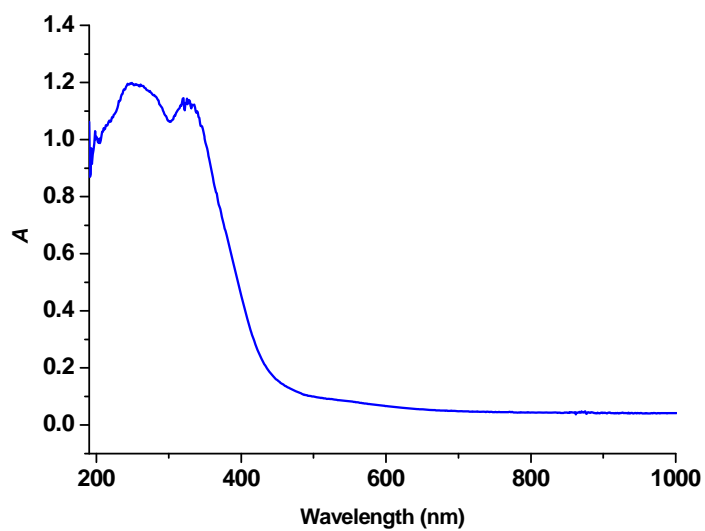


Fig. S7. The UV-Vis spectra of the compound **1P** or **1M** at room temperature.

Table S1 A summary of structure determinations of 11 randomly selected crystals in the products of compound **Zn(Hcapa)(4, 4'-bipy)** from the same crystallization: the R factors and Flack absolute structure parameters for each refinement with the same set of position coordinates.

	a	b	c	R_1	wR_2	Flack parameter	Goodness-of-fit on F^2
1	8.806(2)	9.501(2)	11.490(3)	0.0421	0.0722	0.020(3)	0.997
2	8.806(2)	9.501(2)	11.490(3)	0.0356	0.0723	0.021(1)	1.030
3	8.806(2)	9.501(2)	11.490(3)	0.0614	0.0944	0.041(2)	0.980
4	8.806(2)	9.501(2)	11.490(3)	0.0400	0.0797	-0.010(1)	1.044
5	8.806(2)	9.500(5)	11.490(3)	0.0330	0.0593	0.008(1)	1.014
6	8.806(2)	9.501(2)	11.490(3)	0.0539	0.1078	0.794(2)	1.648
7	8.806(2)	9.501(2)	11.490(3)	0.0554	0.1400	0.94(2)	1.022
8	8.806(2)	9.501(2)	11.490(3)	0.0560	0.1376	0.91(2)	1.019
9	8.806(2)	9.501(2)	11.490(3)	0.0489	0.0928	0.013(1)	1.037
10	8.806(2)	9.501(2)	11.490(3)	0.0434	0.0743	0.011(1)	1.034
11	8.806(2)	9.501(2)	11.490(3)	0.0358	0.0725	0.015(1)	1.022

Table S2 A summary of structure determinations of crystals **6**, **7** and **8** with inverted atomic coordinates.

	A	b	c	R_1	wR_2	Flack parameter	Goodness-of-fit on F^2
6	8.806(2)	9.501(2)	11.490(3)	0.0342	0.0621	0.024(1)	0.990
7	8.806(2)	9.501(2)	11.490(3)	0.0373	0.0759	0.013(1)	1.018
8	8.806(2)	9.501(2)	11.490(3)	0.0381	0.0782	0.011(1)	1.025

References

1. Kurtz, S. K.; Perry, T. T. *J Appl Phys.* 1968, **39**, 3798