Supporting Information

Second-Sphere Coordination-Induced Morphology Transformation from Phosphorescent Nanowires to Microcubes

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Materials

$IrCl_3 \cdot H_2O$ was purchased from Shanghai Jiuyue Chemical Company. 2-phenylpyridine (ppy) was purchased from Shanghai Ruiyi Medical Tech. Co. Ltd. 1,3,5-Benzenedicarboxylic acid was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. 4-bromo-pyridine hydrochloride, ethylene glycol and other agents were obtained from Sinopharm Chemical Reagent Co. Ltd. All solvents were dried by a conventional procedure prior to use. 3,8-dibromophenanthroline,[1] 4-ethynlpyridine[2] and cyclometalated iridium chlorobridged dimmer[3] were synthesized according to the literature, respectively.

General Characterization

^{1}H NMR and ^{13}CNMR spectra were recorded on a Bruker DMX400 NMR spectrometer at room temperature. Mass spectra were tested by the Shimadzu

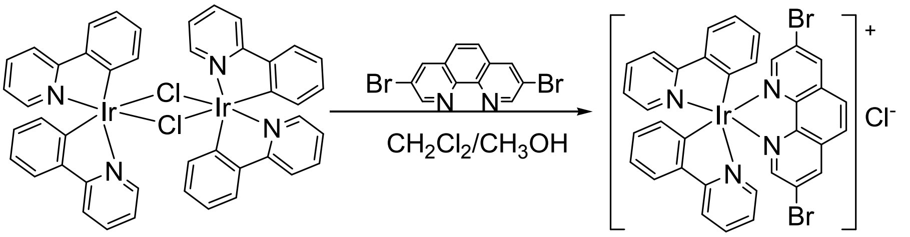
AXIMA-CFRTM plus matrix-assisted laser desorption ionization time-flight mass spectrometry (MALDI-TOF). SEM was determined on a Hitachi S-4800 scanning electron microscope. TEM was determined at 200 kV on a JEOL JEM-2100 transmission electron microscope. EDX was determined on BRUKER QUANTAX 400. XRD diagrams were obtained on an ADVANCE and DAVINCI.DESIGN (Bruker) using a Cu-Kα radiation source (λ = 0.1542 nm). The absorption and emission spectra were recorded using UV-7502PC Xinmao spectrophotometer and Varian Cary Eclipse Fluorescence Spectrophotometer (America), respectively.

X-ray Crystallography Analysis

Diffraction intensity for **1** and **2** are collected (hemisphere technique) on a Bruker SMART Platform CCD diffractometer at 298 K with a molybdenum tube ($\lambda\kappa\alpha$ = 0.71073 Å), and the absorption correction is applied with the SADABS program. The structure solution and full-matrix least-squares refinement based on F2 are performed with the SHELXS-97 and SHELXL-97 program packages, respectively. All the nonhydrogen atoms are refined anisotropically. Analytical expressions of neutral-atom scattering factors are employed, and anomalous dispersion correction incorporated.[4] We used dfix command to restrain the distances. We used isor command to refine the atom isotropically. ISOR was used to restrain atoms which are C51, O5, O6, C50, O4 and O3. There were some guest solvent molecules in the crystals of 1, 2 and they were chemically featureless to refine using conventional discrete-atom models. Therefore the SQUEEZE program implemented in PLATON[5] was used to remove these electron densities. For crystal **1**, the void volume and void count electrons are 2156 and 986. For crystal **2**, the void volume and void count electrons are717 and 163. X-ray crystallographic data in CIF format for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 999600 and No. CCDC 999601. The copies of the available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internet.) + 44-1223/336-033; E-mail:

deposit@ccdc.cam.ac.uk].

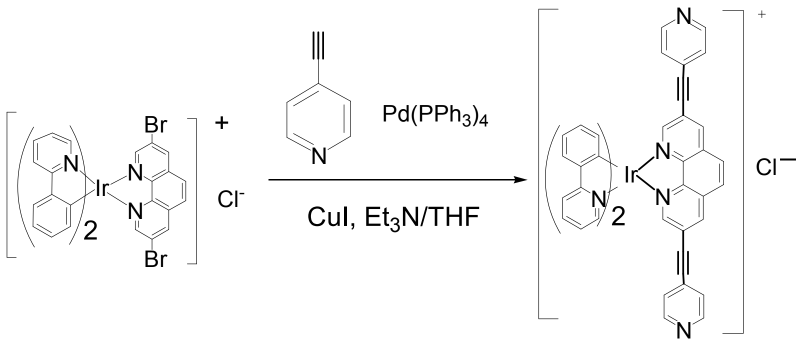
Synthesis of complex 2



(2)

A mixture of [(ppy)$_2$Ir(μ-Cl)$_2$(ppy)$_2$] (0.25 mmol, 267.9 mg) and 3,8-dibromophenanthroline (0.60 mmol, 202.8 mg) was added into a 100 mL three-necked flask. 24 mL of mixed solution of CH_2Cl_2 and CH_3OH (v/v = 2:1) was added. The reaction solution was heated to reflux for 6 h, then cooled to room temperature. The solvent was removed by the vacuum distillation. The crude product was purified by chromatographic column using CH_2Cl_2/methanol (v/v = 50:1) as an eluent to afford a red solid in the yield of 70 %. ^{1}H NMR: (400 MHz, $CDCl_3$), δ (ppm): 9.19 (d, 2 H, *J* = 2.0 Hz), 8.67 (s, 2 H), 8.16 (d, 2 H, *J* = 2.0 Hz), 7.96 (d, 2 H, *J* = 8.0 Hz), 7.79 (t, 2 H, *J* = 7.8 Hz), 7.73 (d, 2 H, *J* = 7.2 Hz), 7.35 (d, 2 H, *J* = 5.6 Hz), 7.09 (t, 2 H, *J* = 7.2 Hz), 6.99 (q, 4 H, *J* = 6.4 Hz), 6.34 (d, 2 H, *J* = 7.2 Hz). MS(MALDI-TOF): *m/z* 839.1 $[M+H]^+$.

Synthesis of complex 1



(1)

A mixture of **2** (1.311 g, 1.5 mmol), Pd(PPh$_3$)$_4$ (104.0 mg, 0.09 mmol), CuI (34.3 mg, 0.18 mmol) and 4-ethynylpyridine (309 mg, 3 mmol) was added into a 100 mL three-necked flask. 20 mL of mixed solution of THF and triethylamine (v/v= 3:1) was added. The mixture was heated to reflux for 10 h, then cooled to room temperature and filtered. The organic phase was dried by anhydrous magnesium sulfate. The solvent was removed by vacuum distillation. The crude product was purified by chromatographic column using CH_2Cl_2/methanol (v/v = 30:1) as an eluent to afford a red solid in the yield of 40 %. ^{1}H NMR: (400 MHz, DMSO), δ (ppm): 9.23 (d, 2 H, J = 1.6 Hz), 8.69 (s, 4 H), 8.43 (s, 2 H), 8.27 (d, 2 H, J = 8.4 Hz), 8.15 (d, 2 H, J = 2.0 Hz), 7.96 (d, 2 H, J = 7.6 Hz), 7.90 (t, 2 H, J = 7.4 Hz), 7.67 (d, 2 H, J = 5.6 Hz), 7.54 (d, 4 H, J = 4.0 Hz), 7.07 (t, 2 H, J = 7.4 Hz), 6.98 (m, 4 H), 6.27 (d, 2 H, J = 7.2 Hz). MS(MALDI-TOF): *m/z* 883.3 $[M+H]^+$.

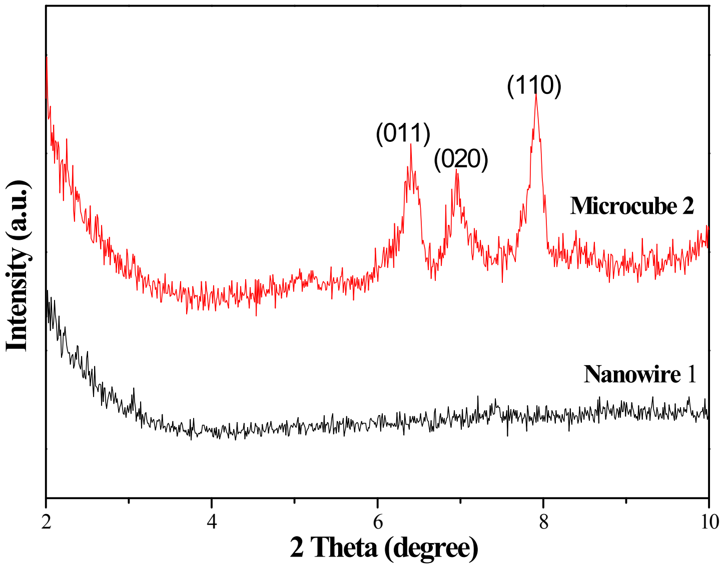


Fig. S1 X-ray profiles of nanowire **1** (black) and microcube **2** (red)

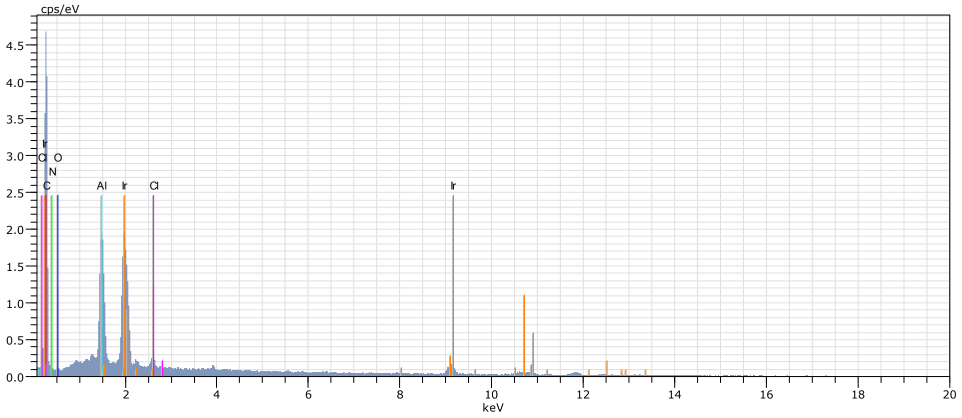


Fig. S2 EDX for nanowire **1**

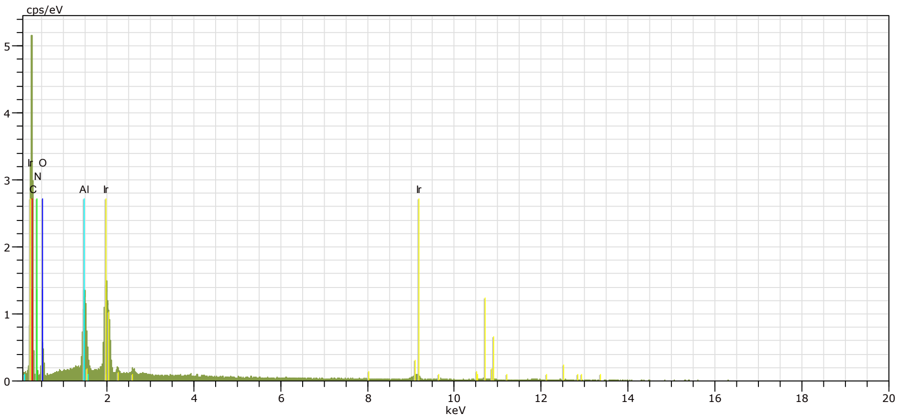


Fig. S3 EDX for and microcube **2**

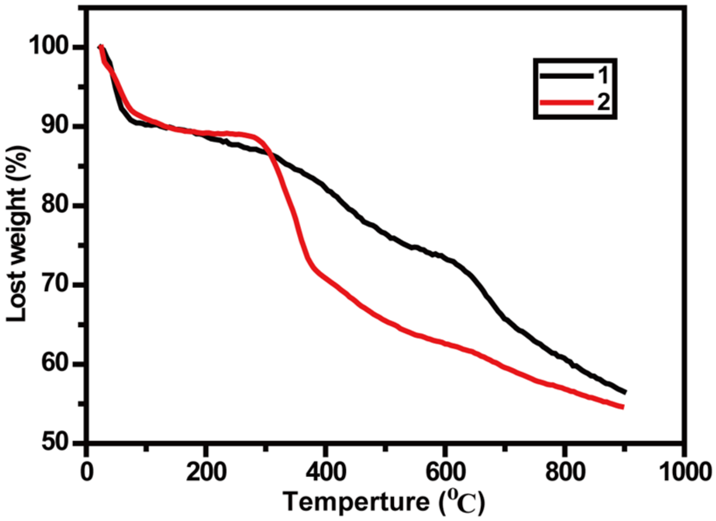


Fig. S4 The TGA thermograms for crystal **1** and **2** under N_2 atmosphere.

Comment: 1 and 2 exhibited the similar weight loss of (~10%) below the 200 ^{o}C. For 1, there are one CH_3CN and two CH_3OH molecules in the asymmetric unit. This is little different from the result from SQUEEZE, which may due to the residual electrons on the iridium center during the SQUEEZE procedure. For 2, there are two CH_3CN and two CH_3OH molecules in the asymmetric unit, which agree well with the result from SQUEEZE.

Table S1 Crystallographic data for **1** and **2.**

	1	**2**
Empirical formula	$C_{48}H_{30}ClIrN_6$	$C_{57}H_{35}IrN_6O_6$
Crystal system	monoclinic	monoclinic
space group	P 21/c	P 21/c
Crystal size	0.20×0.15×0.1	0.28×0.26×0.22
a, Å	12.1796(17)	12.5702(2)
b, Å	26.148(4)	25.9873(4)
c, Å	17.534(3)	17.7066(3)
α(deg)	90°	90.00°
β (deg)	104.082(2)°	102.355(2) °
γ(deg)	90°	90.00°
V, $Å^3$	5416.4(13)	5650.18(16)
Z	4	4
Calculated density, $g\cdot cm^3$	1.126 g/cm^3	1.284 g/cm^3
F(000)	1816	2176
R_1 [I>2σ(I)]	0.0721	0.0612
R_2 [I>2σ(I)]	0.1677	0.1595
wR_1(all data)	0.1047	0.0689
wR_2(all data)	0.1764	0.1635
GOF on F^2	1.070	1.064

Table S2. Selected bond distances of **1** and **2**

	Ir-C(C^N)	Ir-N(C^N)	Ir-N(N^N)
1	2.001(8)	2.044(9)	2.147(8)
	2.015(11)	2.049(9)	2.151(8)
2	1.999(6)	2.038(6)	2.142(5)
	2.002(7)	2.040(6)	2.159(5)

References

1. W. J. Li, H. M. Wu, Y. B. Li, C. P. Hu, M. D. Yi, L. H. Xie, L. Chen, J. F. Zhao, X. H. Zhao, N. E. Shi, Y. Qian, C. Wang, W. Wei and W. Huang, *Tetrahedron*, 2012, 68, 8216-8221.
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