Supporting Information

Phosphorescent polymeric nanomaterials with metallophilic $d^{10} \cdots d^{10}$ interactions self-assembled from $[Au(NHC)_2]^+$ and $[M(CN)_2]^-$

Yong Chen,^{ab} Gang Cheng,^{ac} Kai Li,^a Deepak P. Shelar,^b Wei Lu*^{ad} and Chi-Ming Che*^{ac}

^a State Key Laboratory of Synthetic Chemistry, Institute of Molecular Functional Materials, HKU-CAS Joint Laboratory on New Materials, and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, P. R. China

E-mail: cmche@hku.hk

^b Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

^c HKU Shenzhen Institute of Research and Innovation, Shenzhen 518053, P. R. China

^d Department of Chemistry, South University of Science and Technology of China, 1088 Tangchang Road, Shenzhen, Guangdong 518055, P. R. China

E-mail: <u>luw@sustc.edu.cn</u>

Experimental Section

All starting materials were purchased from commercial sources and used as received. PEDOT:PSS (Clevios P) was purchased from Heraeus, PVK from Sigma-Aldrich, and TPBi from Luminescence Technology Corp. The solvents used for synthesis were of analytical grade unless stated otherwise. Twice-distilled water was used for nanostructure preparations. The precursors **1a** and **1b** were prepared according to a literature method.¹

Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Electrospray Ionization (ESI) mass spectra were obtained on a Finnigan LCQ quadrupole ion trap mass spectrometer (samples were dissolved in HPLC grade methanol). ¹H NMR spectra were recorded with Bruker DRX 300 and Avance 400 FT-NMR spectrometers. Elemental analyses were performed by Beijing Institute of Chemistry, Chinese Academy of Sciences. Infrared spectra were recorded on a Bio-Rad FT-IR spectrometer. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Steady-state emission spectra were obtained on a SPEX 1681 Fluorolog-2 Model F111 fluorescence spectrophotometer equipped with a Hamamatsu R928 PMT detector. Emission lifetime measurements were performed with a Quanta-Ray Q-switch DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). For measuring absolute solid-state emission quantum yield, an integrating sphere F-3018 (HORIBA JOBIN YVON) was equipped to the SPEX 1681 Fluorolog-2 Model F111 spectrophotometer.

 ⁽a) H. M. J. Wang, C. Y. L. Chen and I. J. B. Lin, *Organometallics*, 1999, 18, 1216–1223; (b) R. Rubbiani, I. Kitanovic, H. Alborzinia, S. Can, A. Kitanovic, L. A. Onambele, M. Stefanopoulou, Y. Geldmacher, W. S. Sheldrick, G. Wolber, A. Prokop, S. Wölfl and I. Ott, *J. Med. Chem.*, 2010, 53, 8608–8618.

TEM and SAED were performed on a Philips Tecnai G2 20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. The TEM images and SAED patterns were taken by Gatan MultiScan Camera Model 794. TEM samples were prepared by depositing a few drops of suspensions on the formvar-coated copper grids and the excess solvent was removed by a piece of filter paper. The SEM images were taken on a Hitachi S-4800 field emission scanning electron microscope operating at 5.0 kV. SEM samples were prepared by drop-casting suspensions onto silicon wafers. Gold sputtering was applied before SEM observations. AFM images were recorded on a MFP-3D Stand Alone Atomic Force Microscope (Asylum Research, Oxford Instruments) in the tapping mode with a standard etched silicon probe.

The powder XRD patterns were recorded on a Bruker D8 Powder X-ray Diffractometer operating with graphite monochromatized CuK_{α} radiation ($\lambda = 1.54056$ Å) and a nickel filter. The scanning rate was 0.5° min⁻¹ in the 2 θ range from 3 to 50°.

Single crystals of **1a**, **1b**, **2a** and **3b** suitable for X-ray structure analysis were obtained by vapor diffusion of diethyl ether into methanol or DMF solutions over the period of several days. The diffraction data were collected at 100 (for **1a**, **1b**, **2a**) and 296 (for **3b**) K on a Bruker X8 PROTEUM single crystal X-ray diffractometer with MicroStar rotating-anode X-ray source (CuK_{α} radiation, $\lambda = 1.54178$ Å).

Device fabrication and characterization. Glass slides with pre-patterned ITO electrodes used as substrates of PLEDs were cleaned in an ultrasonic bath of Decon 90 detergent and deionized water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of deionized water, acetone, and isopropanol, and subsequently dried in an oven for 1 h. They were then treated in an ultraviolet-ozone chamber for 20 min before spin-coating PEDOT:PSS. PEDOT:PSS were spin-coated onto the cleaned ITO-coated glass substrate and baked at 120 °C

for 20 min to remove the residual water solvent in a clean room. Blends of PVK:**2b** were spincoated from chlorobenzene atop the PEDOT:PSS layer inside a N₂-filled glove box. The thickness for all EMLs was about 60 nm. Afterwards, all devices were annealed at 110 °C for 10 min inside the glove box and subsequently transferred into a Kurt J. Lesker SPECTROS vacuum deposition system without exposing to air. Finally, TPBi (40 nm), LiF (0.5 nm), and Al (100 nm) were deposited by thermal evaporation at a pressure of 10^{-8} mbar. EL spectra, luminance, and CIE coordination were measured by a Photo Research Inc PR-655. Voltage-current characteristics were measured by a Keithley 2400 source measurement unit. All devices were characterized at room temperature without encapsulation.

Synthesis and Characterization

1a: MS (ESI): m/z 389.2 [M⁺]. ¹H NMR (300 MHz, CD₃OD): δ 7.31 (s, 4H), 3.91 (s, 12H).

1b: MS (ESI): m/z 489.2 [M⁺]. ¹H NMR (400 MHz, CD₃OD): δ 7.76 (m, 4H), 7.57 (m, 4H), 4.21 (s, 12H).

Mixing equivalent moles of the chloride salts of $[Au(NHC)_2]^+$ complexes **1a/1b** and $K[M(CN)_2]$ (M = Au or Ag) in aqueous solutions gave homo- or heteronuclear double salts. The precipitated solid was filtered out and washed thoroughly with water, methanol and diethyl ether. A quantitative yield was achieved for each of the complexes. Due to their polymeric nature, the double salts in the present work are insoluble in common organic solvents, such as methanol, dichloromethane, chloroform, benzene, acetonitrile, acetone, THF, etc., except for hot DMF or DMSO.

2a: MS (FAB): m/z 389.1 [M⁺], 249.0 [M⁻]. ¹H NMR (400 MHz, DMSO-d₆): δ 7.51 (s, 4H), 3.92 (s, 12H). Elemental analysis Calcd for C₁₂H₁₆Au₂N₆: C, 22.58; H, 2.53; N, 13.17. Found: C, 22.14; H, 2.19; N, 13.05. IR (KBr): v = 2135 (C=N) cm⁻¹.

2b: MS (FAB): m/z 489.1 [M⁺], 249.0 [M⁻]. ¹H NMR (400 MHz, DMF-d₇): δ 7.89 (m, 4H), 7.60 (m, 4H), 4.28 (s, 12H). Elemental analysis Calcd for C₂₀H₂₀Au₂N₆: C, 32.53; H, 2.73; N, 11.38. Found: C, 32.07; H, 2.42; N, 11.18. IR (KBr): v = 2137 (C=N) cm⁻¹.

3a: MS (FAB): m/z 389.1 [M⁺]. ¹H NMR (400 MHz, DMF-d₇): δ 7.51 (s, 4H), 3.92 (s, 12H). Elemental analysis Calcd for C₁₂H₁₆AgAuN₆: C, 26.25; H, 2.94; N, 15.30. Found: C, 25.59; H, 2.58; N, 15.10. IR (KBr): v = 2129 (C=N) cm⁻¹.

3b: MS (FAB): m/z 489.1 [M⁺]. Elemental analysis Calcd for C₂₀H₂₀AgAuN₆: C, 37.00; H, 3.10; N, 12.95. Found: C, 36.53; H, 2.87; N, 12.72. IR (KBr): v = 2130 (C=N) cm⁻¹. This complex is insoluble in common organic solvents and decomposes in hot DMF or DMSO solutions, and hence no satisfactory ¹H NMR spectra were recorded. For reference, the following data are reported from an unclean spectrum: ¹H NMR (400 MHz, DMF-d₇): δ 7.89 (m, 4H), 7.60 (m, 4H), 4.28 (s, 12H).



Figure S1. Shading AFM image of the x-shaped nanostructure of **2a** deposited on a glass slide. A typical measurement on the thickness of the nanostructures is also shown.



Figure S2. SEM micrographs depicting the morphological changes of **2a** upon varying the concentration of the precursor **1a** from (left) 0.25 mg, (center) 0.5 mg, to (right) 1.0 mg.



Figure S3. SEM micrographs of superstructures of **2b** (left) and **3b** (right) prepared in water in the absence of the surfactant PEG2000.



Figure S4. Solid-state emission spectra of **1a** and **1b** at 298 K. $\lambda_{ex} = 350$ nm.



Figure S5. AFM images of PVK:**2b** thin films on ITO/PEDOT:PSS with the concentration of **2b** varying from 0 to 25 wt%.



Figure S6. Transmission electron micrographs with higher magnifications of the nanobelts in an aqueous suspension of **1b** reveals that each nanobelt is constructed from parallel-aligned nanowires.



Figure S7. Supplementary ¹H NMR spectra of the polymeric double salts in hot DMF or DMSO.

Concentration	Max.	Max. current	Max. power	Max.	CIE coordinates at
(wt%)	luminance	efficiency	efficiency	EQE (%)	$100 \text{ cd/m}^2 (x, y)$
	(cd/m^2)	(cd/A)	(lm/W)		
2.5	670	1.54	0.81	1.45	(0.168, 0.134)
10	720	1.00	0.63	1.02	(0.168, 0.128)
25	180	0.69	0.38	0.66	(0.173, 0.135)

Table S1. Key performances of PLEDs based on the emission of **2b**.