Supporting Information

Self-assembled Nanostructures with Tridentate Cyclometalated Platinum(II) Complexes

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Experimental Section

Synthesis and Spectroscopic Characterization:

All starting materials were used as received from commercial sources. The ligand 6-(4’-methylphenyl)-2,2’-bipyridine (HC^N=NC) was prepared according to literature methods. Elemental analyses were performed by the Institute of Chemistry at Chinese Academy of Sciences, Beijing. 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 CH₃CN). $^1$H, $^{13}$C, $^{31}$P, $^{19}$F
and $^{195}$Pt NMR spectra were recorded on Avance400 and 500 Bruker FT-NMR spectrometers with chemical shifts (in ppm) relative to tetramethylsilane (for $^1$H and $^{13}$C NMR) and external H$_3$PO$_4$ (for $^{31}$P NMR) respectively. Infrared spectra were recorded on a Bio-Rad FT-IR spectrometer. UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer.

$^{[(C^\text{N}^\text{N})PtCl]}$ (2). A mixture of 6-(4'-methylphenyl)-2,2'-bipyridine (HC$^\text{N}^\text{N}$) (192 mg, 0.78 mmol) and K$_2$PtCl$_4$ (300 mg, 0.72 mmol) in CH$_3$CN/H$_2$O (1:1 v/v, 50 mL) was refluxed for 18 hours. The resulted dark red solution was evaporated to dryness under reduced pressure. The residue was extract with CH$_2$Cl$_2$ (100 mL $\times$ 3) and the extracts was evaporated to dryness. Pure product (250 mg, yield 73%) was isolated as an orange solid by slow diffusion of Et$_2$O vapor into a concentrated DMF solution. Anal. Calcd for C$_{17}$H$_{13}$ClN$_2$Pt: C, 42.94; H, 2.76; N, 5.90. Found: C, 43.10; H, 2.47; N, 6.27. MS (+ve FAB): $m/z$ 475 [M$^+$], 440 [M$^+$ – Cl]. $^1$H NMR ($d_6$-DMSO): $\delta$ 8.86 (d, 1H, $J = 5.0$ Hz), 8.45 (d, 1H, $J = 7.9$ Hz), 8.31 (t, 1H, $J = 7.7$ Hz), 8.13–8.10 (m, 2H), 7.88 (t, 1H, $J = 6.0$ Hz), 7.86 (t, 1H, $J = 7.4$ Hz), 7.45 (d, 1H, $J = 7.7$ Hz), 7.28 (s with $^{195}$Pt satellites, 1H, $J_{\text{PH}} = 43.6$ Hz), 6.87 (d, 1H, $J = 7.7$ Hz), 2.28 (s, 3H).
Figure S1. $^1$H NMR spectrum of $\mathbf{2}$ in $d_6$-DMSO.

$[(\text{C}^\text{N}^\text{N})\text{PtC}=\text{O}](\text{PF}_6)$ (3). A mixture of $\mathbf{2}$ (100 mg, 0.21 mmol) and AgOTf (60 mg, 0.23 mmol) in CH$_3$CN (30 mL) was refluxed for 2 hours. The resulted suspension was filtered through celite when it was still hot. Orange micro-needles precipitated out when the filtrate was cooled down. This precipitate was proved to be $[(\text{C}^\text{N}^\text{N})\text{PtN}=\text{C}CH_3]$(OTf). X-ray crystallographic study on a single crystal of $[(\text{C}^\text{N}^\text{N})\text{PtN}=\text{C}CH_3](\text{PF}_6)$ has revealed that the $[(\text{C}^\text{N}^\text{N})\text{PtN}=\text{C}CH_3]^{+}$ moieties are linked by Pt⋯Pt interactions into a dimeric structure in the solid state. The details will be reported elsewhere. To the hot (50 °C) solution of $[(\text{C}^\text{N}^\text{N})\text{PtN}=\text{C}CH_3](\text{OTf})$ in CH$_3$CN was bubbled carbon monoxide (CO) gas for 10 minutes and the resulted yellow solution was stirred overnight at room temperature under a CO atmosphere. The solvent was
evaporated to dryness and the resulted orange solid was dissolved with 20 mL CH$_3$OH. The CH$_3$OH solution was filtered into a saturated NH$_4$PF$_6$ solution in CH$_3$OH. The resulted orange-brown solid was collected on sinter-glass filter and washed with copious of water, CH$_3$OH and Et$_2$O. Recrystallization by slow diffusion of Et$_2$O into a concentrated CH$_3$CN solution yielded orange-brown solid (85 mg, 66%). Anal. Caled for C$_{18}$H$_{13}$N$_2$OPtPF$_6$: C, 35.23; H, 2.14; N, 4.57. Found: C, 35.71; H, 2.45; N, 4.15. MS (+ve FAB): m/z 468 [M$^+$.] IR (KBr): $\nu$ = 2109 (C≡O) cm$^{-1}$. $^1$H NMR ($d_6$-DMSO): $\delta$ 8.99 (d, 1H, $J$ = 4.9 Hz), 8.47–8.43 (m, 2H), 8.20 (t, 1H, $J$ = 7.9 Hz), 8.15 (d, 1H, $J$ = 7.7 Hz), 7.97 (t, 1H, $J$ = 8.0 Hz), 7.88 (t, 1H, $J$ = 6.0 Hz), 7.51 (d, 1H, $J$ = 7.8 Hz), 6.94 (d, 1H, $J$ = 7.8 Hz), 6.81 (s with $^{195}$Pt satellites, 1H, $J_{PtH} = 44$ Hz), 2.08 (s, 3H).

Figure S2. $^1$H NMR spectrum of 3 in $d_6$-DMSO.
Figure S3. IR absorption spectrum of 3 in KBr pellet.

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\text{\{[(C}^\text{N}^\text{N})\text{PtCl}][\text{[(C}^\text{N}^\text{N})\text{PtC=O}]\text{)](PF}_6\text{)} \text{ (1). Two methods were applied to prepare this complex.}
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\text{Method I (serendipity approach): To a solution of 2 (120 mg, 0.25 mmol) in CH}_2\text{Cl}_2 \text{ (120 mL) was bubbled CO gas for 20 minutes. The resulted dark green solid was collected on a sinter-glass filter and washed thoroughly with CH}_2\text{Cl}_2 \text{ and Et}_2\text{O. The solid (75 mg) was dissolved with DMF (1.5 mL) in the presence of NH}_4\text{PF}_6 \text{ (20 mg). The resulted dark red solution was filtered into water (30 mL) to give a dark blue precipitate which was collected on a sinter-glass filter and washed thoroughly with water, CH}_3\text{OH, CH}_2\text{Cl}_2 \text{ and Et}_2\text{O. Yield: 48% based on 2.}
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Method II (rational approach): The mixture of 2 (19.0 mg, 0.04 mmol) and 3 (24.5 mg, 0.04 mmol) in CH$_3$CN (5 mL) was stirred for 10 minutes. The resulted red solution was filtered and evaporated to dryness to give a dark blue solid which was collected on a sinter-glass filter and washed thoroughly with CH$_3$OH, CH$_2$Cl$_2$ and Et$_2$O. Yield: >80%.

Anal. Calcd for C$_{35}$H$_{26}$N$_4$ClOPt$_2$PF$_6$: C, 38.60; H, 2.41; N, 5.15. Found: C, 37.71; H, 2.04; N, 4.65. MS (ESI): $m/z$ 942.5 [M$^+$], 468.1 {M$^+$ – [(C=N=N)PtCl]}. IR (KBr): $\nu$ = 2094 (C≡O) cm$^{-1}$. $^1$H NMR (d$_6$-DMSO): $\delta$ 8.87 (d, 1H, $J$ = 5.0 Hz), 8.80 (d, 1H, $J$ = 4.9 Hz), 8.31 (d, 1H, $J$ = 7.7 Hz), 8.25 (d, 1H, $J$ = 7.5 Hz), 8.14 (virtual d, 2H), 8.02 (t, 1H, $J$ = 8.0 Hz), 7.97–7.80 (m, 4H), 7.76 (d, 1H, $J$ = 7.8 Hz), 7.68 (d, 1H, $J$ = 8.2 Hz), 7.54 (d, 1H, $J$ = 7.9 Hz), 7.23 (d, 1H, $J$ = 7.8 Hz), 7.14 (d, 1H, $J$ = 7.8 Hz), 6.85 (d, 1H, $J$ = 7.9 Hz), 6.74 (d, 1H, $J$ = 5.6 Hz), 6.70 (s with $^{195}$Pt satellites, 1H), 6.30 (s with $^{195}$Pt satellites, 1H), 2.09 (s, 3H), 2.06 (s, 3H). $^1$H NMR (CD$_3$CN): $\delta$ 8.66 (d, 1H, $J$ = 4.2 Hz), 8.55 (d, 1H, $J$ = 4.4 Hz), 7.97 (t, 1H, $J$ = 7.8 Hz), 7.92 (t, 1H, $J$ = 7.8 Hz), 7.61 (t, 1H, $J$ = 8.0 Hz), 7.56 (t, 1H, $J$ = 5.4 Hz), 7.52 (t, 1H, $J$ = 5.5 Hz), 7.49 (t, 1H, $J$ = 7.9 Hz), 7.41 (d, 1H, $J$ = 8.5 Hz), 7.39 (d, 1H, $J$ = 8.1 Hz), 7.11 (d, 1H, $J$ = 7.8 Hz), 7.00 (t, 1H, $J$ = 7.3 Hz), 6.91 (d, 1H, $J$ = 7.9 Hz), 6.68–6.62 (m, 3H), 6.55 (d, 1H, $J$ = 7.9 Hz), 6.28 (s with $^{195}$Pt satellites, 1H), 5.85 (s with $^{195}$Pt satellites, 1H), 2.09 (s, 3H), 1.88 (s, 3H). $^{13}$C{$^{1}$H} NMR (CD$_3$CN): $\delta$ 207.8 (C≡O), 169.6, 165.7, 164.4, 157.7, 156.9, 155.7, 155.2, 154.9, 148.8, 144.4, 144.3, 143.9, 143.7, 143.1, 141.7, 141.5, 140.5, 139.5, 138.5, 137.4, 134.7, 129.1, 128.7, 127.9, 127.0, 125.6, 125.0, 124.1, 120.9, 120.5, 119.8, 119.6, 22.2 (Me), 21.8 (Me). $^{195}$Pt{$^{1}$H} NMR (CD$_3$CN): $\delta$ –3832.7 (virtual s). $^{19}$F{$^{1}$H} NMR (CD$_3$CN): $\delta$ –72.5 (d, $J_{PF}$ = 708 Hz). $^{31}$P{$^{1}$H} NMR (CD$_3$CN): $\delta$ –144.5 (virtual quintet, $J_{PF}$ = 706 Hz).
Figure S4. $^1$H NMR spectrum of 1 in CD$_3$CN.

Figure S5. 2D H-H COSY NMR spectrum of 1 in CD$_3$CN.
Figure S6. 2D NOESY NMR spectrum of 1 in CD$_3$CN.

Figure S7. $^{13}$C NMR spectrum of 1 in CD$_3$CN.
Figure S8. $^{195}$Pt NMR spectrum of I in CD$_3$CN.

Figure S9. $^{31}$P NMR spectrum of I in CD$_3$CN.
Figure S10. $^{19}$F NMR spectrum of 1 in CD$_3$CN.

Figure S11. $^1$H NMR spectrum of 1 in $d_6$-DMSO.
Figure S12. $^1$H NMR spectrum of 1 in $d_6$-acetone (nanowire dispersion with concentration being $\sim 2 \times 10^{-3}$ M).

Figure S13. IR absorption spectrum of 1 in KBr pellet.
Supporting Information

Figure S14. ESI-MS spectrum of 1 in CD$_3$CN.

Figure S15. Experimental and stimulated (inset) isotopic pattern of [(C$^\text{N}^\text{N}$N)PtC≡O]$^+$ (C$_{18}$H$_{13}$N$_2$OPt).
Figure S16. Experimental and stimulated (inset) isotopic pattern of $\{(\text{C}^\text{N}^\text{N})\text{PtCl}\} [(\text{C}^\text{N}^\text{N})\text{PtC}=\text{O}]^+$ (C$_{35}$H$_{26}$N$_4$Cl$_2$O$_2$Pt$_2$).

Figure S17. UV-vis absorption spectra of 1 dispersed in various poor solvents (prepared by injecting 100 µL 1.2 × 10$^{-3}$ M acetone solution into 10 mL poor solvent).
TEM, SEM and FET Devices:

TEM images and SAED pictures were recorded on a Philips Tecnai 20 electron microscope (accelerating voltage of 200 kV). The SEM images were taken on a LEO 1530 scanning electron microscope operating at 5.0 kV. A few drops of the nanowire dispersion were deposited on the copper grid and the excess solvent was removed by a piece of filter paper. All the samples for SEM observations were sputtered with gold thin film (20 second, <2 nm thickness).

The XRD pattern of the nanostructured thin film was recorded on a Philips PW1830 powder X-ray diffractometer operating with graphite monochromatized Cu K\(\alpha\) radiation (\(\lambda = 1.540562 \text{ Å}\)) and nickel filter. The scanning rate is 0.5° min\(^{-1}\) in the 2\(\theta\) range from 2 to 70°.

A common substrate-gate structure field effect transistor (FET) was fabricated. The SiO\(_2\) layer (100 nm, relative permittivity = 3.9), heavily doped n-type Si substrates, Ti adhesion film (10 nm, lower)/Au conductive film (50 nm, upper) were used as the insulator, gate electrode and source/drain electrodes, respectively. The transistor output and transfer characteristics were measured with a probe station under nitrogen atmosphere using a Keithley K4200 semiconductor parameter analyzer. The transistor channel length and widths were 5 and 1035 \(\mu\text{m}\) respectively.
**Figure S18.** TEM image of 1 dispersed in acetone (concentration $\sim 6 \times 10^{-3}$ M).

**Figure S19.** SEM image of 1 dispersed in acetone (concentration $\sim 6 \times 10^{-3}$ M).
Figure S20. TEM image of 1 dispersed in various poor solvents.
**Figure S21.** Transfer ($I_{DS}$ vs. $V_G$) characteristics of the TFT device with nanostructured 1 as semiconducting layer.

**Figure S22.** Transient measurement ($V_{DS} = V_G = 20$ V) of the TFT device with nanostructured 1 as semiconducting layer.