Supplementary information for

A ^{195}Pt NMR Study on Zero-Magnetic-Field Splitting and the Phosphorescence Properties in the Excited Triplet States of Cyclometalated Platinum(II) Complexes

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Preparations and Characterizations of 1Pt – 3Pt.

Chemicals and Characterizations. Potassium tetrachloroplatinate and benzo[h]quinoline (bhq) were purchased from Wako Pure Chemical Co., Ltd. 2-Phenylpyridine (ppy), acetylacetone (acac), and dipivaloylmethane (dpm) were obtained from Tokyo Chemical Industry Co., Ltd. All of these chemicals were used as received without further purification. 2-(2-Thienyl)pyridine (thpy) was prepared according to the literature.[1] Electron spray ionization mass spectroscopy (ESI-MS) and FT $^{1}H/^{195}Pt$ NMR measurements were conducted by using a micromassZQ spectrometer (Waters Co.) and a 400 MHz JNM-ECZ spectrometer (JEOL Ltd.), respectively. For ^{1}H and ^{195}Pt NMR spectroscopies, tetramethylsilane (in $CDCl_3$, 0 ppm) and potassium tetrachloroplatinate (in D_2O, –1618 ppm with respect to hexachloroplatinate) were used as internal and external standards, respectively, for determining the chemical shifts of the NMR signals in ppm.

Synthesis of Platinum(II) Complexes [Pt(C^N)(O^O)] (1Pt–3Pt). [Pt(C^N)(O^O)] complexes (**1Pt**–**3Pt**) were prepared by a microwave-assisted method as described below.[2] A C^N cyclometalate ligand (bhq, thpy, or ppy, 0.241 mmol) was dissolved in 10 mL of a 2-ethoxyethanol/water solution (3/1 = v/v) of K_2PtCl_4 (100 mg, 0.241 mmol). The solution deaerated by purging an Ar gas stream was heated at 60°C for 1 min under microwave irradiation (150–200 W) and, then, the mixture was cooled immediately to room temperature by an ice bath. After the heating-cooling procedures mentioned above being performed three times, 20 mL of water was added dropwise to the solution. The yellow ~ green precipitates were collected by filtration and dried in vacuo. The chloro-bridged dimer as the product was used for the following reaction without further purification. The powder of the chloro-bridged dimer (1 eq.) was suspended in 10 mL of a 2-ethoxyethanol/water mixture (3/1 = v/v) in the presence of both CH_3COONa (10 eq.) and 2 eq. of dipivaloylmethane (**1Pt**) or acetylacetone (**2Pt** and **3Pt**). The mixture deaerated by purging an Ar gas stream was heated at 60°C for 10 min under microwave irradiation (150–200 W). An addition of an excess amount of water to the reaction mixture yielded yellow ~ green precipitates. The precipitates washed thoroughly with water were dried and

purified by silica-gel column chromatography with dichloromethane as an eluent. The eluent was concentrated by evaporation and, then, methanol was diffused slowly to the solution, yielding the yellow ~ green crystals.

[Pt(bhq)(dpm)] (1Pt): Yield = 43 mg (32%). ^{1}H NMR ($CDCl_3$, ppm) δ = 9.12 (d, 1H), 8.27 (d, 1H), 7.82–7.75 (m, 2H), 7.58 (d, 2H), 7.52 (d, 1H), 7.45 (dd, 1H), 5.87 (s, 1H), 1.32 (d, 18H). ^{195}Pt NMR ($CDCl_3$, ppm) δ = –2770. ESI-MS (CH_3CN) for $PtC_{24}H_{27}NO_2$: *m*/*z* 556 ($[M+H]^+$).

[Pt(thpy)(acac)] (2Pt): Yield = 26 mg (24%). ^{1}H NMR ($CDCl_3$, ppm) δ = 8.80 (d, 1H), 7.67 (td, 1H), 7.49 (d, 1H), 7.29 (t, 1H), 7.20 (d, 1H), 6.92 (td, 1H), 5.48 (s, 1H), 2.00 (d, 6H). ^{195}Pt NMR ($CDCl_3$, ppm) δ = –2790. ESI-MS (CH_3CN) for $PtC_{14}H_{13}NO_2S$: *m*/*z* 454 ($[M+H]^+$).

[Pt(ppy)(acac)] (3Pt): Yield = 31 mg (29%). ^{1}H NMR ($CDCl_3$, ppm) δ = 9.00 (d, 1H), 7.80 (td, 1H), 7.62 (d, 2H), 7.44 (dd, 1H), 7.21 (td, 1H), 7.13–7.08 (m, 2H), 5.48 (s, 1H), 2.01 (d, 6H). ^{195}Pt NMR ($CDCl_3$, ppm) δ = –2870. ESI-MS (CH_3CN) for $PtC_{16}H_{15}NO_2$: *m*/*z* 448 ($[M+H]^+$).

References

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