## Supporting Information for

# Highly Polar Solvent-induced Disproportionation of a Cationic Pt(II)-Diimine Complex Containing an *o*-Semiquinonato

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#### **General Procedures.**

All synthetic operations were performed under an atmosphere of N<sub>2</sub> using Schlenk-line techniques. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and chloroform (CHCl<sub>3</sub>) were purchased from Wako Pure Chemical Industries 4,4'-Di-*tert*-butyl-2,2'-bipyridine (Japan). (DTBbpy), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), and 3,5-di-tert-butylbenzoquinone (3,5-DTBBQ) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan). Ethanol (EtOH), dimethyl sulfoxide (DMSO), toluene, tetrahydrofuran (THF), methanol (MeOH), N,N-dimethylformamide (DMF), n-hexane, and chloroform- $d_1$  with 0.03% TMS, were purchased from Kanto Chemical Co., Inc. (Japan). Ferrocenium hexafluorophosphate ( $Fc^+PF_6^-$ ) and tetrabutylammonium chloride (TBACl) were purchased from Sigma-Aldrich Chemicals. N,N-Dimethylformamide- $d_7$  with 1 v/v% TMS (DMF- $d_7$ ) and dimethyl sulfoxide- $d_6$  with 0.03 v/v% TMS (DMSO- $d_6$ ) were purchased from Acros Organics. Purified water by a Millipore milli-Q system yielding 10 M  $\Omega$  cm was used as H<sub>2</sub>O. [PtCl<sub>2</sub>(DTBbpy)] and [Pt(3,5-DTBCat)(DTBbpy)] (1) were synthesized by the literature methods except for using NaOH instead of t-BuOK.<sup>1,2</sup> All of the solvents for the syntheses and the measurements were finally degassed in three freeze-pump-thaw cycles at least just prior to use.

### Synthetic procedure of [Pt(3,5-DTBSQ)(DTBbpy)]PF<sub>6</sub> (1(PF<sub>6</sub>)).<sup>2</sup>

An 21 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to a mixure of [Pt(3,5-DTBCat)(DTBbpy)] (1) (148.06 mg, 0.217 mmol) and Fc<sup>+</sup>PF<sub>6</sub><sup>-</sup> (73.16 mg, 0.221 mmol) afforded bluish purple solution. The mixture was stirred at room temperature for 3 h, affording a dark green solution. The dark green solid after evaporation was washed with H<sub>2</sub>O until the filtrate becomes colorless. Then, the solid was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and concentrated to about 10 mL. Addition of 30 mL of *n*-hexane afforded dark green precipitate. The dark green precipitate was washed with *n*-hexane and dried in vacuo. Complex 1(PF<sub>6</sub>) was isolated as dark green powder in 67% yield. Anal. Found: C, 46.52; H, 5.45; N, 3.28. Calcd. for  $C_{32}H_{44}PtN_2O_2PF_6$  (1(PF<sub>6</sub>)): C, 46.38; H, 5.35; N, 3.38.  $\chi_M T_{299 \text{ K}} = 0.347 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ .

#### **Physical Measurements.**

Elemental analysis was carried out on a PerkinElemer 2400 II CHN series. Electrochemical measurements were carried out with a BAS model 650A electrochemical analyzer. A standard threeelectrode system (a glassy carbon working electrode, platinum-wire counter electrode, and Ag/Ag<sup>+</sup> /CH<sub>3</sub>CN electrode as reference) was used for CV studies in solution. UV-Vis-NIR spectra were recorded on a Hitachi U-4100 spectrophotometer over the range 200–3300 nm under an atmosphere of N<sub>2</sub>. Temperature dependent absorption spectra were measured with a CoolSpeK USP-203. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a Smart-Orbit (Diamond) ATR accessory. <sup>1</sup>H NMR (500 MHz) spectra were measured in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>, and DMF-*d*<sub>7</sub> with a JEOL ECA 500 MHz spectrometer. The signals from the residual solvent protons of CDCl<sub>3</sub> (7.26 ppm), DMSO-*d*<sub>6</sub> (2.50 ppm), DMF-*d*<sub>7</sub> (8.02 ppm) were used as internal standards.<sup>3</sup> Magnetic susceptibility in CDCl<sub>3</sub> solution at 299 K were determined by the Evans' Method,<sup>4</sup> using 500 MHz spectrometer and 5 mm Coaxial Insert NMR tube. The concentration of the samples was kept 1 mM. All values were corrected for diamagnetism using Pascal's constants.<sup>5</sup> Electrospray ionization mass spectra (ESI-MS) were measured by a JEOL JMS-T100LC AccuTOF spectrometer under an atmosphere of N<sub>2</sub>.

solvent	$\lambda / \operatorname{nm} (\varepsilon / \operatorname{cm}^{-1} \operatorname{M}^{-1})^a$
Complex 1	
МеОН	289 (23,600), 357 (2,090), 527 (4,130)
EtOH	291 (23,600), 365 (2,020), 548 (3,980)
DMSO	296 (26,300), 372 (2,270), 564 (4,910)
DMF	296 (26,700), 375 (2,190), 575 (5,190)
CHCl <sub>3</sub>	297 (23,200), 389 (2,210), 614 (4,570)
THF	299 (25,200), 396 (2,150), 634 (5,370)
Toluene	304 (21,400), 412 (2,110), 649sh (4,830), <sup>b</sup> 696 (5,270)
Complex $1(PF_6)$	
MeOH	303 (12,400), 461 (6,030), 588 (2,800)
EtOH	296 (12,900), 462 (5,510), 492sh (4,440), 587 (2,730)
CHCl <sub>3</sub>	305 (12,700), 464 (6,590), 593 (2,880)
THF	307 (12,900), 463 (5,900), 494sh (4,590), 597 (2,870)
Toluene	312 (11,600), 463 (4,970), 502sh (3,880), 613 (2,660), 673sh (1,820)

Table S1. UV-vis-NIR spectral data of 1 and  $1(PF_6)$  in several solvents at 298 K

<sup>*a*</sup> measured using 0.1 mM solutions. <sup>*b*</sup> sh = shoulder



Figure S1. IR spectra of a) 1 and b)  $1(PF_6)$  in the solid state.

The characteristic C–O vibration made for the SQ ligand in  $1(PF_6)$  appears at 1574 cm<sup>-1.2</sup> The comparison of these spectra supports the presence of SQ ligand in  $1(PF_6)$ .



**Figure S2.** Cyclic voltammograms of a) **1** and b)  $\mathbf{1}(PF_6)$  in  $CH_2Cl_2$  (1 mM, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, under N<sub>2</sub>, 100 mV/s) and c) the redox scheme.



**Figure S3.** Correlation of the Pt(NN)(SS) solvent parameter<sup>6</sup> and absorption maxima of a) **1** and b)  $1(PF_6)$ , in several solvents, with a liner least-squares fits. The fitting results are included in each figure.



**Figure S4.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in toluene (0.1 mM) and b) time courses of absorbances at 463 ( $\bullet$ ) and 696 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S5.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in CHCl<sub>3</sub> (0.1 mM) and b) time courses of absorbances at 464 ( $\bullet$ ) and 614 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S6.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in THF (0.1 mM) and b) time courses of absorbances at 463 ( $\bullet$ ) and 634 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S7.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in MeOH (0.1 mM) and b) time courses of absorbances at 461 ( $\bullet$ ) and 527 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S8.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in EtOH (0.1 mM) and b) time courses of absorbances at 462 ( $\bullet$ ) and 548 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S9.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in DMF (0.1 mM) and b) time courses of absorbance at 575 ( $\blacktriangle$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S10.** a) Absorption spectra of **1** (–) and **1**(PF<sub>6</sub>) ((– (0 h), – (10 h), – (20 h)) in DMSO (0.1 mM) and b) time courses of absorbance at 564 ( $\bullet$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S11.** a) Absorption spectra of **1** (– (0 h), – (6 h), – (12 h)) in DMF (0.1 mM) and b) time courses of absorbance at 575 ( $\bullet$ ) nm at 323 K. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.



**Figure S12.** a) Absorption spectra of **1** ((– (0 h), – (6 h), – (12 h)) in DMSO (0.1 mM) and b) time courses of absorbance at 564 ( $\bullet$ ) nm. Each first data point at 0 h was measured at 298 K then the temperature was increased to 323 K.

a)



**Figure S13.** <sup>1</sup>H NMR spectra of a)  $1(PF_6)$  after heating at 323 K in DMSO- $d_6$  for 2 h, b) 1, c) 3,5-DTBBQ, d) DMSO- $d_6$  after heating at 323 K in DMSO- $d_6$  for 2 h in the presence of 2 eq. *n*-Bu<sub>4</sub>NCl, and e) [PtCl<sub>2</sub>(DTBbpy)] in DMSO- $d_6$ .



**Figure S14.** <sup>1</sup>H NMR spectra of a)  $1(PF_6)$  after heating at 323 K in DMF- $d_7$  for 2 h, b) 1, c) 3,5-DTBBQ, d) DMF- $d_7$  after heating at 323 K in DMF- $d_7$  for 2 h in the presence of 2 eq. *n*-Bu<sub>4</sub>NCl, and e) [PtCl<sub>2</sub>(DTBbpy)] in DMF- $d_7$ . The peaks marked by \* are assigned as residual proton of DMF- $d_7$ .



**Figure S15.** a) Positive-mode ESI-MS spectrum of DMSO- $d_6$  solution of **1**(PF<sub>6</sub>) after heating at 323K and diluted in THF. b) The observed (black lines) and c) simulated spectra (blue lines).

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