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# Synthesis and Characterization of Luminescent Osmium (II) Carbonyl Complexes Based on Chelating Dibenzoylmethane and Halide Ligands

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## Supporting Information

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## Experimental Section

*General information and Materials.* All synthetic manipulations were performed under N<sub>2</sub> atmosphere using standard Schlenk technique. All solvents prior to use were dried via appropriate technique. Os<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub> was synthesized by reacting the suspension of Os<sub>3</sub>(CO)<sub>12</sub> in hexane with 1.5 eq. of I<sub>2</sub> in autoclave at 175°C for 24 h following literature procedure. Os<sub>2</sub>(CO)<sub>6</sub>(tfa)<sub>2</sub> was also prepared from a toluene suspension of Os<sub>3</sub>(CO)<sub>12</sub> and trifluoroacetic acid in autoclave at 180°C for 6 hours. Dibenzoylmethane (dbm)H was purchased from TCI, Tokyo Kasei Kogyo Co. Ltd, Japan. All other chemicals used in this work were of reagent grade and were used without further purification.

Elemental analyses and Mass spectra (operating in EI and FAB mode) were carried out at the NSC Regional Instrument Centre at National Chiao Tung University, Taiwan. IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 400 or an Inova-500 MHz instrument; chemical

shifts are quoted with respect to internal standard Me<sub>4</sub>Si. Cyclic voltammetric measurements were carried out on a voltammetric analyzer, CH Instruments, model 830 with Pt-disk milli working electrode; Pt-wire auxiliary and Ag/AgCl reference electrode; at scan rate 0.1 V/s. Verification of voltammogram nature was carried out by varying the scan rate from 0.05 to 0.5 V/s. The voltammograms were recorded in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte at 0.1 M concentration, whereas the solute concentration was maintained at 10<sup>-3</sup> M under N<sub>2</sub> atmosphere. Potential was checked by using ferrocene as a standard reference at 0.45 V under the same experimental condition. Number of electrons involved in the redox process was counted on comparing with current height of standard ferrocene solution.

Electronic (UV-VIS) absorption spectra were recorded on a Hitachi U3300 spectrophotometer. Emission spectra were recorded under degassed condition (using at least three freeze-pump-thaw cycles) on a Perkin Elmer F4500 fluorescence spectrophotometer. Emission quantum yields were measured at excitation wavelength λ<sub>exc</sub> = 380 nm in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Coumarin-1 (Φ<sub>r</sub> = 0.60 in EtOH) was used as the reference, and the equation:

$$\Phi_s = \Phi_r \left( \frac{\eta_s^2 A_r I_s}{\eta_r^2 A_s I_r} \right)$$

was used to calculate the emission quantum yields, where Φ<sub>s</sub> and Φ<sub>r</sub> are the quantum yield of unknown and reference sample, η is the refractive index of the solvent, A<sub>r</sub> and A<sub>s</sub> are the absorbance of the reference and the unknown sample at the excitation wavelength, and I<sub>s</sub> and I<sub>r</sub> are the integrated areas under the emission spectra of interest, respectively.

For the lifetime measurements, the third harmonic of a Nd:YAG laser 355 nm with duration 10 ns was used. Emission decay was detected by a photomultiplier tube and averaged over 500 shots using an oscilloscope. Each decay curve consists of 2500 data points. Laser energy was reduced to < 1 mJ/pulse to prevent possible photochemical decomposition. For the short lifetime component, a 50 ps diode laser at wavelength 375 nm combining the time-

correlated signal photon counting set up was used. The instrument response function is ~ 130 ps.

*Synthesis of Os(CO)<sub>3</sub>(tfa)(dbm) (1).* To a 30 mL Carius tube, it was charged with Os<sub>2</sub>(CO)<sub>6</sub>(tfa)<sub>2</sub> (200 mg, 0.26 mmol) and dibenzoylmethane (dbm)H (130 mg, 0.58 mmol). The tube was sealed under vacuum and placed into an oven maintained at 180 °C for 6 hours. After the reaction was completed, the tube was cooled, opened and the content was subjected to sublimation at 175 °C and 200 mtorr. Further purification was carried out by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and hexane, giving 227 mg of primrose yellow compound [Os(CO)<sub>3</sub>(tfa)(dbm)] (0.37 mmol, 72 %).

Spectral data of **1**: MS (EI, <sup>192</sup>Os), m/z 612 (M<sup>+</sup>), 556 (M – 2CO)<sup>+</sup>, 528 (M – 3CO)<sup>+</sup>. IR(C<sub>6</sub>H<sub>12</sub>): ν(CO), 2125 (s), 2047 (vs), 2031 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>, 298 K): δ 8.15 (d, J<sub>HH</sub> = 7.4 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 7.64 (t, J<sub>HH</sub> = 7.4 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.54 (t, J<sub>HH</sub> = 7.4 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 7.26 (s, CH, 1H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>, 298 K): δ 182.9 (CO, 2C), 169.7 (CO, C), 168.9 (CO, 2C), 162.5 (q, <sup>2</sup>J<sub>CF</sub> = 38 Hz, C(CF<sub>3</sub>)), 138.2 (*i*-C<sub>6</sub>H<sub>5</sub>, 2C), 133.5 (*p*-C<sub>6</sub>H<sub>5</sub>, 2C), 129.6 (*m*-C<sub>6</sub>H<sub>5</sub>, 2C), 128.8 (*o*-C<sub>6</sub>H<sub>5</sub>, 2C), 115.8 (q, <sup>1</sup>J<sub>CF</sub>=287 Hz, CF<sub>3</sub>), 97.0 (CH). <sup>19</sup>F NMR (470.3 MHz, acetone-d<sub>6</sub>, 298 K): δ –73.94 (s 3F). Anal. Calcd for C<sub>20</sub>H<sub>11</sub>F<sub>3</sub>O<sub>7</sub>Os: C, 39.35; H, 1.82. Found: C, 39.28; H, 2.40.

*Synthesis of [Os(CO)<sub>3</sub>(Cl)(dbm)](2).* A mixture of [Os(CO)<sub>3</sub>(tfa)(dbm)] (100 mg, 0.16 mmol) and LiCl (28 mg, 0.66 mmol) in methanol (25 mL) was heated to reflux for 4 h. After then, the solvent was evaporated in vacuum, and the residue was washed with water, filtered and dried. The dried mass was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and methanol, giving bright yellow solid [Os(CO)<sub>3</sub>(Cl)(dbm)]. Yield: 74 mg, 0.14 mmol, 85%.

Spectral data of **3**: MS (EI, <sup>192</sup>Os), m/z 534 (M<sup>+</sup>), 478 (M – 2CO)<sup>+</sup>, 450 (M – 3CO)<sup>+</sup>. IR (C<sub>6</sub>H<sub>12</sub>): ν (CO), 2118 (s), 2038 (vs), 2022 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.95 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 7.54 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.45 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 6.92 (s, 1H, CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ 181.9 (2C,

C(C<sub>6</sub>H<sub>5</sub>)), 167.9 (2C, CO), 166.5 (1C, CO), 137.6 (2C, *i*-C<sub>6</sub>H<sub>5</sub>), 132.4 (2C, *p*-C<sub>6</sub>H<sub>5</sub>), 128.5 (4C, *o*, *m*-C<sub>6</sub>H<sub>5</sub>), 127.7 (4C, *m*, *o*-C<sub>6</sub>H<sub>5</sub>), 96.9 (1C, CH). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>ClO<sub>5</sub>Os: C, 40.56; H, 2.08. Found: C, 40.61; H, 2.25.

*Synthesis of Os(CO)<sub>3</sub>(Br)(dbm) (3)*. A mixture of [Os(CO)<sub>3</sub>(tfa)(dbm)] (100 mg, 0.16 mmol) and NaBr (70 mg, 0.68 mmol) in 25 mL of methanol was heated to reflux for 4 hours, affording 74 mg of light yellow [Os(CO)<sub>3</sub>(Br)(dbm)] (0.13 mmol, 78%) after recrystallization.

Spectral data of **3**: MS (EI, <sup>192</sup>Os), m/z 578 (M<sup>+</sup>), 522 (M – 2CO)<sup>+</sup>, 494 (M – 3CO)<sup>+</sup>. IR (C<sub>6</sub>H<sub>12</sub>): ν (CO), 2117 (s), 2038 (vs), 2022 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.94 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 7.54 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.45 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 6.92 (s, 1H, CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ 182.0 (2C, C(C<sub>6</sub>H<sub>5</sub>)), 167.9 (2C, CO), 165.6 (1C, CO), 137.6 (2C, *i*-C<sub>6</sub>H<sub>5</sub>), 132.4 (2C, *p*-C<sub>6</sub>H<sub>5</sub>), 128.6 (4C, *o*, *m*-C<sub>6</sub>H<sub>5</sub>), 127.7 (4C, *m*, *o*-C<sub>6</sub>H<sub>5</sub>), 97.3 (1C, CH). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>BrO<sub>5</sub>Os: C, 37.44; H, 1.92. Found: C, 37.58; H, 2.08.

*Synthesis of [Os(CO)<sub>3</sub>(I)(dbm)] (4)*. Procedures identical to that of **1** were followed, using 200 mg of Os<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub> (0.25 mmol) and 123 mg of dibenzoylmethane (0.55 mmol). Purification was conducted using vacuum sublimation (96 °C and 200 mtorr) and recrystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane, giving 201 mg of yellow complex [Os(CO)<sub>3</sub>I(dbm)] (0.32 mmol, 70 %).

Spectral data of **4**: MS (EI, <sup>192</sup>Os), m/z 626 (M<sup>+</sup>), 570 (M – 2CO)<sup>+</sup>, 542 (M – 3CO)<sup>+</sup>. IR (C<sub>6</sub>H<sub>12</sub>): ν (CO), 2113 (s), 2035 (vs), 2022 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>, 298 K): δ 7.92 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 7.54 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.45 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 6.92 (s, 1H, CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ 182.3 (2C, C(C<sub>6</sub>H<sub>5</sub>)), 168.4 (2C, CO), 163.9 (1C, CO), 137.7 (2C, *i*-C<sub>6</sub>H<sub>5</sub>), 132.3 (2C, *p*-C<sub>6</sub>H<sub>5</sub>), 128.5 (4C, *o*, *m*-C<sub>6</sub>H<sub>5</sub>), 127.6 (4C, *m*, *o*-C<sub>6</sub>H<sub>5</sub>), 98.1 (1C, CH). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>IO<sub>5</sub>Os: C, 34.62; H, 1.87. Found: C, 34.77; H, 1.90.

Selected crystal data:  $C_{18}H_{11}IO_5Os$ ,  $M = 624.37$ , monoclinic, space group  $P 2_1/n$ ,  $a = 9.5934(6)$ ,  $b = 10.4791(7)$ ,  $c = 37.126(2)$  Å,  $\beta = 93.86(0)$  °,  $V = 3723.9(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 2.227$  gcm<sup>-3</sup>,  $F(000) = 2304$ , crystal size  $0.20 \times 0.10 \times 0.10$  mm,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å,  $T = 293(2)$  K,  $\mu = 8.530$  mm<sup>-1</sup>, 23439 reflections collected, 8955 unique ( $R_{\text{int}} = 0.0448$ ), final  $wR_2(\text{all data}) = 0.0848$ .  $R_1[I > 2\sigma(I)] = 0.0450$ .

*Synthesis of [Os(CO)<sub>3</sub>(SCN)(dbm)] (5).* A mixture of  $[\text{Os}(\text{CO})_3(\text{tfa})(\text{dbm})]$  (100 mg, 0.16 mmol) and  $\text{NH}_4\text{SCN}$  (50 mg, 0.66 mmol) in 25 mL of methanol was heated to reflux for 4 hours. The product was purified by extraction and recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol, giving 70 mg of light yellow solid  $[\text{Os}(\text{CO})_3(\text{SCN})(\text{dbm})]$  (0.13 mmol, 77%).

Spectral data of **5**: MS (EI, <sup>192</sup>Os),  $m/z$  555 ( $M^+$ ), 499 ( $M - 2\text{CO}$ )<sup>+</sup>, 471 ( $M - 3\text{CO}$ )<sup>+</sup>. IR ( $C_6H_{12}$ ):  $\nu$  (CN), 2073 (br);  $\nu$  (CO), 2124 (s), 2041 (vs), 2035 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.93 (d, <sup>3</sup> $J_{\text{HH}} = 7.5$  Hz, 4H,  $C_6H_5$ ), 7.57 (t, <sup>3</sup> $J_{\text{HH}} = 8.0$  Hz, 2H,  $C_6H_5$ ), 7.47 (t, <sup>3</sup> $J_{\text{HH}} = 8.0$  Hz, 4H,  $C_6H_5$ ), 6.95 (s, 1H, CH). <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  182.4 (2C,  $C(C_6H_5)$ ), 168.9 (1C, SCN), 166.0 (2C, CO), 161.5 (1C, CO), 137.0 (2C, *i*- $C_6H_5$ ), 132.7 (2C, *p*- $C_6H_5$ ), 128.7 (4C, *o*, *m*- $C_6H_5$ ), 127.8 (4C, *m*, *o*- $C_6H_5$ ), 97.1 (1C, CH). Anal. Calcd for  $C_{19}H_{11}NO_5OsS$ : C, 41.07; N, 2.52; H, 2.00. Found: C, 41.02; N, 2.28; H, 2.16.