ESI for

A diphenylamino-substituted cationic cyclometalated Ir(III) complex: its aggregation-induced phosphorescent emission and oxygen sensing properties

Lei Wang, a Zhanming Gao, a Chun Liu, * a Xin Jin b

a State Key Laboratory of Fine Chemicals, Dalian University of Technology, Linggong Road 2, 116024, Dalian, China; E-mail: cliu@dlut.edu.cn
b Eco-chemical Engineering Cooperative Innovation Center of Shandong, Qingdao University of Science and Technology, Qingdao 266042, China.

Contents


Fig. S1 – S4. Photophysical and electrochemical properties of iridium(III) complexes. Page S3 - S4

Fig. S5 - S8. Electron density maps and Stern-Volmer plots of oxygen sensing properties of iridium(III) complexes. Page S5 - S6.

Fig. S9 - S13. NMR and HRMS spectra of iridium(III) complexes. Page S7 - S9.
**Ir1**, Yield 71%, yellow solid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.90 (d, $J$ = 8.2 Hz, 2H), 8.39 (s, 2H), 8.26 (d, $J$ = 8.1 Hz, 2H), 8.20 (d, $J$ = 4.9 Hz, 2H), 8.05 (dd, $J$ = 8.2, 5.1 Hz, 2H), 7.95 (d, $J$ = 7.7 Hz, 2H), 7.87 (t, $J$ = 7.8 Hz, 2H), 7.46 (d, $J$ = 5.7 Hz, 2H), 7.06 (t, $J$ = 7.5 Hz, 2H), 7.02 - 6.91 (m, 4H), 6.29 (d, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 171.49, 156.26, 153.60, 153.25, 151.46, 151.33, 142.86, 141.88, 136.27, 134.64, 133.50, 132.39, 130.96, 130.85, 130.61, 129.06, 127.26, 127.15, 124.15, 124.03, 119.09. HRMS (MALDI-TOF, m/z): calcd for C$_{58}$H$_{42}$N$_6$Ir [M - PF$_6$]$^+$ 1015.3100, found: 1015.3111.

**Ir2**, Yield 62%, yellow solid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.89 (dd, $J$ = 8.2, 1.2 Hz, 2H), 8.42 - 8.32 (m, 4H), 8.13 (dd, $J$ = 8.2, 5.1 Hz, 2H), 7.80 (d, $J$ = 8.3 Hz, 2H), 7.72 (d, $J$ = 8.7 Hz, 2H), 7.49 - 7.42 (m, 2H), 7.25 (t, $J$ = 7.9 Hz, 8H), 7.05 (t, $J$ = 7.4 Hz, 6H), 6.98 (d, $J$ = 7.6 Hz, 8H), 6.55 (dd, $J$ = 8.6, 2.3 Hz, 2H), 6.53 - 6.46 (m, 2H), 5.88 (d, $J$ = 2.3 Hz, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 171.49, 156.26, 153.60, 153.25, 151.46, 151.33, 142.86, 141.88, 136.27, 134.64, 133.50, 132.39, 130.96, 130.85, 130.61, 129.06, 127.26, 127.15, 124.15, 124.03, 119.09. HRMS (MALDI-TOF, m/z): calcd for C$_{58}$H$_{42}$N$_6$Ir [M - PF$_6$]$^+$ 1015.3100, found: 1015.3111.
Fig. S1 Emission spectra of Ir(III) complexes Ir1 and Ir2 in EC film at room temperature ($\lambda_{ex}$ = 410 nm).

Fig. S2 Phosphorescence decay profiles of Ir1 and Ir2 in CH$_2$Cl$_2$ at room temperature.
Table S1 The photoluminescence quantum yields ($\Phi_{\text{PL}}$) of complexes \textbf{Ir1} and \textbf{Ir2} in different states

<table>
<thead>
<tr>
<th></th>
<th>Photoluminescence quantum yields ($\Phi_{\text{PL}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In CH$_3$CN</td>
</tr>
<tr>
<td>\textbf{Ir1}</td>
<td>3.1%</td>
</tr>
<tr>
<td>\textbf{Ir2}</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

\textbf{Fig. S3} The photoluminescence quantum yields ($\Phi_{\text{PL}}$) of complex \textbf{Ir2} ($5.0 \times 10^{-5}$ M) in H$_2$O/CH$_3$CN with different water fractions (0-90%) at room temperature.

\textbf{Fig. S4} Cyclic voltammograms of Ir(III) complexes \textbf{Ir1} and \textbf{Ir2} in CH$_2$Cl$_2$ ($1.0 \times 10^{-3}$ M).
**Fig. S5** Electron density maps of **Ir1** and **Ir2** calculated by a TD-DFT approach.

**Fig. S6** Stern-Volmer plots (intensity ratios $I_0/I$ versus O$_2$ partial pressure) of **Ir1** and **Ir2** in CH$_2$Cl$_2$ ($1.0 \times 10^{-5}$ M).
Fig. S7 Variation of the emission intensity of \textit{Ir1} and \textit{Ir2} immobilized in EC films with the oxygen concentrations.

Fig. S8 Response times and relative intensity change for \textit{Ir1} (left) and \textit{Ir2} (right) immobilized in EC films on switching between 100% nitrogen and 100% oxygen for 4000 s.
Fig. S9 The $^1$H NMR spectrum of Ir1 in DMSO-$d_6$.

Fig. S10 The $^1$H NMR spectrum of Ir2 in DMSO-$d_6$. 
Fig. S11 The $^{13}$C NMR spectrum of Ir2 in DMSO-$d_6$.

Fig. S12 The HRMS spectrum of cationic portion of Ir2.
Fig. S13 The MS spectrum of PF$_6^-$.