Electronic Supplementary Information (ESI)

A simple strategy to achieve remarkable mechanochromism of cationic Ir(III) phosphors through subtle ligand modification

Kai-Yue Zhao,a Hui-Ting Mao,a Li-Li Wen,a Guo-Gang Shan,*a Qiang Fu,*a Hai-Zhu Suna and Zhong-Min Sun*ab

a Institute of Functional Material Chemistry and National & Local United Engineering Lab for Power Battery, Faculty of chemistry, Northeast Normal University, Changchun, Jilin130024, P. R. China

E-mail: shangg187@nenu.edu.cn (G. G. Shan), fuq863@nenu.edu.cn (Q. Fu), zmsu@nenu.edu.cn (Z. M. Su).

b School of Chemistry & Environmental Engineering, Changchun University of Science and Technology, Changchun, Jilin 130012, P. R. China
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Synthetic routes and characteristic of ancillary ligands L1-L4

Scheme S1. Synthetic routes of the ancillary ligands L1-L4. Scheme S1 exhibits the synthetic routes of the ancillary ligands L1-L4. 2-(3-methyl-1H-1,2,4-triazol-5-yl)pyridine, the intermediate Inter-1 and ancillary ligand L2, L4 were synthesized according to the modified reported procedures.\(^1,2\)

**3-bromo-9-(4-(3-methyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)butyl)-9H-carbazole (L1).**

Compound L1 was prepared according to the procedure described for L2. Yield: 66%.

\(^1\)H NMR (500 MHz, CDCl\(_3\), ppm): \(\delta\) 8.53 (d, \(J= 4.5\) Hz, 1H), 8.14–8.17 (m, 2H), 8.01 (d, \(J= 7.5\) Hz, 1H), 7.80 (t, \(J= 7.5\) Hz, 1H), 7.44–7.50 (m, 2H), 7.37 (d, \(J= 8.5\) Hz, 2H), 7.29–7.31 (m, 1H), 7.21–7.26 (m, 2H), 4.78 (t, \(J= 7.0\) Hz, 2H), 4.30 (t, \(J= 7.0\) Hz, 2H), 2.44 (s, 3H), 1.93–2.05 (m, 2H), 1.88–1.91 (m, 2H). MS (ESI): calcld for \(\text{[C}_{24}\text{H}_{22}\text{BrN}_{5}]^{+}\) m/z 460.1137, found 460.1131. Anal. Calcld for \(\text{C}_{24}\text{H}_{22}\text{BrN}_{5}\): C, 62.61; H, 4.82; N, 15.21. Found: C, 62.54; H, 4.75; N, 15.29.

**3-methyl-9-(4-(3-methyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)butyl)-9H-carbazole (L3).**

Compound L3 was prepared according to the procedure described for L2. Yield: 68%.

\(^1\)H NMR (500 MHz, CDCl\(_3\), ppm): \(\delta\) 8.52–8.55 (m, 1H), 8.15 (d, \(J= 7.5\) Hz, 1H), 8.04 (d, \(J= 7.5\) Hz, 1H), 7.88 (s, 1H), 7.78–7.81 (m, 1H), 7.40–7.42 (m, 1H), 7.34 (d, \(J= 8.5\) Hz, 1H), 7.29–7.31 (m, 2H), 7.24–7.28 (m, 2H), 7.17–7.20 (m, 1H), 4.75–4.80 (m,
2H), 4.26–4.33 (m, 2H), 2.52 (d, \(J = 7.0\) Hz, 3H), 2.44 (d, \(J = 3.5\) Hz, 3H), 1.95–2.01 (m, 2H), 1.88–1.93 (m, 2H). MS (ESI): calcd for \([\text{C}_{24}\text{H}_{25}\text{N}_5]\) ([M+H]+) m/z 396.2188, found 396.2183. Anal. Calcd for \(\text{C}_{24}\text{H}_{25}\text{N}_5\): C, 75.92; H, 6.37; N, 17.71. Found: C, 75.85; H, 6.23; N, 17.80.

**Fig. S1** \(^1\)H NMR spectrum of **Ir-CzBr** in DMSO-\(d_6\).

![Fig. S1](image)

**Fig. S2** \(^1\)H NMR spectrum of **Ir-Cz** in DMSO-\(d_6\).

![Fig. S2](image)
Fig. S3 $^1$H NMR spectrum of Ir-CzMe in DMSO-$d_6$.

Fig. S4 $^1$H NMR spectrum of Ir-CzDMe in DMSO-$d_6$. 
Fig. S5 $^{19}$F NMR spectrum of Ir-CzBr in DMSO-$d_6$.

Fig. S6 $^{19}$F NMR spectrum of Ir-Cz in DMSO-$d_6$. 
Fig. S7 $^{19}$F NMR spectrum of Ir-CzMe in DMSO-$d_6$.

Fig. S8 $^{19}$F NMR spectrum of Ir-CzDMe in DMSO-$d_6$. 

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**Fig. S9** (a) Emission spectra of **Ir-Cz** in CH$_3$CN-H$_2$O mixtures with different H$_2$O fractions (0–90%) at room temperature. (b) Plot of relative PL intensity ($I/I_0$) at 489 nm *versus* the composition of CH$_3$CN-H$_2$O mixture of **Ir-Cz**, where $I_0$ = peak intensity in pure CH$_3$CN. Inset: photographs of **Ir-Cz** in pure CH$_3$CN solution and CH$_3$CN-H$_2$O mixture ($f_w$ = 90%) under 365 nm UV illumination.

**Fig. S10** (a) Emission spectra of **Ir-CzMe** in CH$_3$CN-H$_2$O mixtures with different H$_2$O fractions (0–90%) at room temperature. (b) Plot of relative PL intensity ($I/I_0$) at 508 nm *versus* the composition of CH$_3$CN-H$_2$O mixture of **Ir-CzMe**, where $I_0$ = peak intensity in pure CH$_3$CN. Inset: photographs of **Ir-CzMe** in pure CH$_3$CN solution and CH$_3$CN-H$_2$O mixture ($f_w$ = 90%) under 365 nm UV illumination.
Fig. S11 (a) Emission spectra of Ir-CzDMe in CH$_3$CN-H$_2$O mixtures with different H$_2$O fractions (0–90%) at room temperature. (b) Plot of relative PL intensity ($I/I_0$) at 513 nm versus the composition of CH$_3$CN-H$_2$O mixture of Ir-CzDMe, where $I_0 =$ peak intensity in pure CH$_3$CN. Inset: photographs of Ir-CzDMe in pure CH$_3$CN solution and CH$_3$CN-H$_2$O mixture ($f_w = 90\%$) under 365 nm UV illumination.

<table>
<thead>
<tr>
<th>Table S1</th>
<th>Photophysical characteristics of Ir-CzBr, Ir-Cz, Ir-CzMe and Ir-CzDMe.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution $\lambda_{em}$ (nm), $\Phi_F$ (%) $\tau$ (µs)</td>
</tr>
<tr>
<td>Ir-CzBr</td>
<td>494, 1.0, 0.023</td>
</tr>
<tr>
<td>Ir-Cz</td>
<td>497, 0.5, 0.017</td>
</tr>
<tr>
<td>Ir-CzMe</td>
<td>503, 0.4, 0.028</td>
</tr>
<tr>
<td>Ir-CzDMe</td>
<td>488, 0.4, 0.038</td>
</tr>
</tbody>
</table>

$^{a} \lambda_{em}$, emission maximum. $^{b} \Phi_F$, photoluminescence quantum yield measured by an integrating sphere. $^{c} \tau$, photoluminescence lifetime. $^{d} a_{AIE} = \Phi_F$ (solid) / $\Phi_F$ (solution).
Fig. S12 Molecular orbital amplitude plots and energy levels of \textit{Ir-Cz}, \textit{Ir-CzMe} and \textit{Ir-CzDMe}.

Fig. S13 Emission spectra of \textit{Ir-Cz} in various states at room temperature. Inset: the photographs of \textit{Ir-Cz} in various states under 365 nm UV illumination.

Fig. S14 Emission spectra of \textit{Ir-CzDMe} in various states at room temperature. Inset: the photographs of \textit{Ir-CzDMe} in various states under 365 nm UV illumination.
Fig. S15 Maximum emission wavelength changes of **Ir-CzBr** *versus* repeating cycles.

Fig. S16 Maximum emission wavelength changes of **Ir-Cz** *versus* repeating cycles.

Fig. S17 Maximum emission wavelength changes of **Ir-CzDMe** *versus* repeating cycles.
Fig. S18 Powder X-ray diffraction patterns of Ir-CzBr in various states.

Fig. S19 Powder X-ray diffraction patterns of Ir-Cz in various states.

Fig. S20 Powder X-ray diffraction patterns of Ir-CzDMe in various states.
**Fig. S21** Chemical structure of *Ir-CztBut* reported in Ref. 2.

**Fig. S22** The emission spectrum of *Ir-CztBut* in powder at room temperature.

**References**
