Electronic Supporting Information

Scheme S1

BTE-imidazole-py

R =

\[ \text{Me} \]

Scheme S2

BrLH: \( R = \text{Br} \)

PLH: \( R = \text{PO(OEt)}_2 \)

Scheme S3

L2H

hnbdtiH
Scheme S4

Scheme S5 Structure transition of tBuLH (top) and tBuLMeH (bottom) between the open form and the closed form

Table S1 UV-vis absorption bands of tBuLH, tBuLMeH 1 and 2 in CH$_2$Cl$_2$ at room temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBuLH</td>
<td>228, 291, 326</td>
</tr>
<tr>
<td>tBuLMeH</td>
<td>230, 291, 326</td>
</tr>
<tr>
<td>1</td>
<td>248, 379, 450</td>
</tr>
<tr>
<td>2</td>
<td>245, 346, 450</td>
</tr>
</tbody>
</table>
**Table S2** Emission data of tBuLH, tBuLMeH, 1, 2 and [Ir(dfppy)$_2$(L1)]·2CH$_3$OH in CH$_2$Cl$_2$ at room temperature and emission data of 1, 2 and [Ir(dfppy)$_2$(L1)]·2CH$_3$OH in C$_2$H$_5$OH-CH$_3$OH (v/v = 3/1) at 77 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission wavelength (nm) at room temperature</th>
<th>Emission wavelength (nm) at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1H</td>
<td>442 nm$^a$</td>
<td>-</td>
</tr>
<tr>
<td>tBuLH</td>
<td>464 nm</td>
<td>-</td>
</tr>
<tr>
<td>tBuLMeH</td>
<td>479 nm</td>
<td>-</td>
</tr>
<tr>
<td>[Ir(dfppy)$_2$(L1)]·2CH$_3$OH</td>
<td>508 nm$^a$</td>
<td>471, 506 nm$^{a,b}$</td>
</tr>
<tr>
<td>1</td>
<td>514 nm</td>
<td>498 nm</td>
</tr>
<tr>
<td>2</td>
<td>507 nm</td>
<td>492 nm</td>
</tr>
</tbody>
</table>

$^a$: the data from *Dalton Trans.*, 2015, **44**, 4289; $^b$: seeing Fig. S19.

**Fig. S1** $^1$H NMR spectrum of tBuLH (500 MHz, CDCl$_3$).
Fig. S2 $^1$H NMR spectrum of tBuLMeH (300 MHz, CDCl$_3$).

Fig. S3 $^1$H NMR spectrum of 1 (500 MHz, CDCl$_3$).
Fig. S4 $^1$H NMR spectrum of 2 (500 MHz, CDCl$_3$).

Fig. S5 Experimental and simulated XRD patterns of tBuLH-HOAc.
Fig. S6 Experimental and simulated XRD patterns of 1.

Fig. S7 Packing structure of tBuLH-HOAc.
**Fig. S8** Packing structure of \([\text{Ir(dfppy)}_2\text{(L1)}] \cdot 2\text{CH}_3\text{OH}\) containing right- and left-handed helical chains (denoted as R and L, respectively). Red balls are O atoms from \(\text{CH}_3\text{OH}\) molecules or phenolate groups.

**Fig. S9** Electrospray mass spectrometry (ES-MS) of tBuLH in \(\text{CH}_3\text{OH-CH}_2\text{Cl}_2\) solution before UV irradiation (\(\lambda = 326\) nm).
Fig. S10  Electrospray mass spectrometry (ES-MS) of tBuLH in CH$_3$OH-CH$_2$Cl$_2$ solution after 2.5-minute UV irradiation ($\lambda = 326$ nm).

Fig. S11  Plot a: irradiating ($\lambda = 326$ nm) the CH$_2$Cl$_2$ solution of tBuLH ($c = 1.0 \times 10^{-5}$ M) for 2.5 minutes; plots b and c: irradiating ($\lambda = 700$ nm) the solution corresponding to plot a for 1 and 2 minutes, respectively; plot d: placing the solution corresponding to plot a in the dark for 45 minutes.
Fig. S12 $^1$H NMR spectrum of tBuLH after irradiation with 326 nm light (500 MHz, CDCl$_3$).

Fig. S13 Plot a: irradiating ($\lambda = 321$ nm) the CH$_2$Cl$_2$ solution of tBuLMeH ($c = 1.0 \times 10^{-5}$ M) for 2 minutes; plots b and c: irradiating ($\lambda = 570$ nm) the solution corresponding to plot a for 0.5 and 1 minute, respectively; plot d: placing the solution corresponding to plot a in the dark for one hour.
Fig. S14 $^1$H NMR spectrum of tBuLMelH after irradiation with 321 nm light (300 MHz, CDCl$_3$).

Fig. S15 UV-vis absorbance change of tBuLH at 700 nm in CH$_2$Cl$_2$ at room temperature, upon alternative irradiation with 326 and 700 nm light (total 5 cycles).
Fig. S16 UV-vis absorbance change of tBuLMeH at 570 nm in CH$_2$Cl$_2$ at room temperature, upon alternative irradiation with 321 and 570 nm light (total 5 cycles).

Fig. S17 Absorption-spectra changes of hpbdtiH in CH$_2$Cl$_2$-CH$_3$CN (v/v = 1/4) solution ($c = 2.5 \times 10^{-5}$ M) upon UV irradiation ($\lambda = 321$ nm) for 0 - 3 minutes, from the ESI of Chem. Commun., 2013, 49, 8863.
Fig. S18 Phosphorescence spectra of 1 and 2 in C₂H₅OH-CH₃OH (v/v = 3/1) at 77 K (c = 1.5 × 10⁻⁴ M, λₑₓ = 370 nm).

Fig. S19 Phosphorescence spectra of [Ir(dfppy)₂(L1)]·2CH₃OH in C₂H₅OH-CH₃OH (v/v = 3/1) at 77 K (λₑₓ = 405 nm), from the ESI of *Dalton Trans.*, 2015, **44**, 4289.
Fig. S20 Luminescence spectra of tBuLH and tBuLMelH in CH$_2$Cl$_2$ at room temperature before and after three-minute UV irradiation with 326 nm light for the former, and 321 nm light for the latter ($c = 4 \times 10^{-5} \text{ M}, \lambda_{ex} = 340 \text{ nm for 2}$).