Supporting Information

Experimental Section

Apparatus. $^1$H NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer at room temperature with chemical shifts reported relative to tetramethylsilane. Electrospray mass spectra (ESI-MS) were recorded on a Thermo Finnigan LCQ Deca XP max (Finnigan, USA) spectrometer. Elemental analysis of complexes was performed on a Vario MICRO instrument. The absorption spectra were recorded on a Lambda 750 spectrophotometer. Steady-state emission spectra were recorded on a Hitachi fluorescence F-4600 spectrophotometer (PMT: 700V).

The photophysical data of [Ir(pq)$_2$(bpy-sugar)]Cl were listed in Table 1.

Table 1. Photophysical Properties of complexes at Room Temperature

<table>
<thead>
<tr>
<th>complex</th>
<th>$\lambda_{abs}$/nm($\varepsilon$/10$^4$ dm$^3$/mol$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{em}$/nm</th>
<th>$\phi_{em}^a$</th>
<th>$\phi_{ecl}^b$</th>
<th>$\tau$/µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(pq)$_2$(bpy-sugar)]Cl</td>
<td>266 (4.61), 319 (1.81), 336 (1.38), 432 (0.34)</td>
<td>557</td>
<td>0.117 (0.084)</td>
<td>5.3</td>
<td>1.02 (0.53)</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]Cl$_2$</td>
<td>610$^i$</td>
<td>0.042$^i$ (0.028$^2$)</td>
<td>1.0</td>
<td>0.64$^i$ (0.48)</td>
<td></td>
</tr>
</tbody>
</table>

The data of complexes were measured at 298 K. $^a$The excitation wavelength for the complex was 430 nm. The luminescence quantum yields were calculated using [Ru(bpy)$_3$]Cl$_2$ in degassed aqueous solution as the standard. The data in ( ) were measured in aerated aqueous solution. $^b$Relative ECL efficiency vs. [Ru(bpy)$_3$]$^{2+}$ (1.0), TPrA (20 mM) in phosphate buffer (0.1 M, pH = 7.5).

Reference:

Figure S1. $^1$H NMR spectrum of [Ir(pq)$_2$(bpy-sugar)]Cl in DMSO-d$_6$ at 25°C.

Figure S2. ESI-MS spectrum of [Ir(pq)$_2$(bpy-sugar)]Cl
Fig. S3 ECL signals of the [Ir(pq)$_2$(bpy-sugar)]$^+$ (a) and [Ru(bpy)$_3$]$^{2+}$ (b) at a GC electrode in 0.15 M PBS (pH 7.5) containing 5 μM complex and 1 mM TPA. Scan rate: 0.1 V s$^{-1}$. 