

Supporting Information

Experimental Section

Apparatus. ^1H 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 $[\text{Ir}(\text{pq})_2(\text{bpy-sugar})]\text{Cl}$ were listed in Table 1.

Table 1. Photophysical Properties of complexes at Room Temperature

complex	$\lambda_{\text{abs}}/\text{nm} (\varepsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{\text{em}}/\text{nm}$	$\varphi_{\text{em}}^{\text{a}}$	$\varphi_{\text{ecl}}^{\text{b}}$	$\tau/\mu\text{s}$
$[\text{Ir}(\text{pq})_2(\text{bpy-sugar})]\text{Cl}$	266 (4.61), 319 (1.81), 336 (1.38), 432 (0.34)	557	0.117 (0.084)	5.3	1.02 (0.53)
$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	—	610 ¹	0.042 ¹ (0.028 ²)	1.0	0.64 ¹ (0.48)

The data of complexes were measured at 298 K. ^aThe excitation wavelength for the complex was 430 nm. The luminescence quantum yields were calculated using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in degassed aqueous solution as the standard. The data in () were measured in aerated aqueous solution.

^bRelative ECL efficiency vs. $[\text{Ru}(\text{bpy})_3]^{2+}$ (1.0), TPrA (20 mM) in phosphate buffer (0.1 M, pH = 7.5).

Reference:

- 1 J. Van Houten, R. J. Watts, *J. Am. Chem. Soc.* **1976**, *98*, 4853.
- 2 K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 269

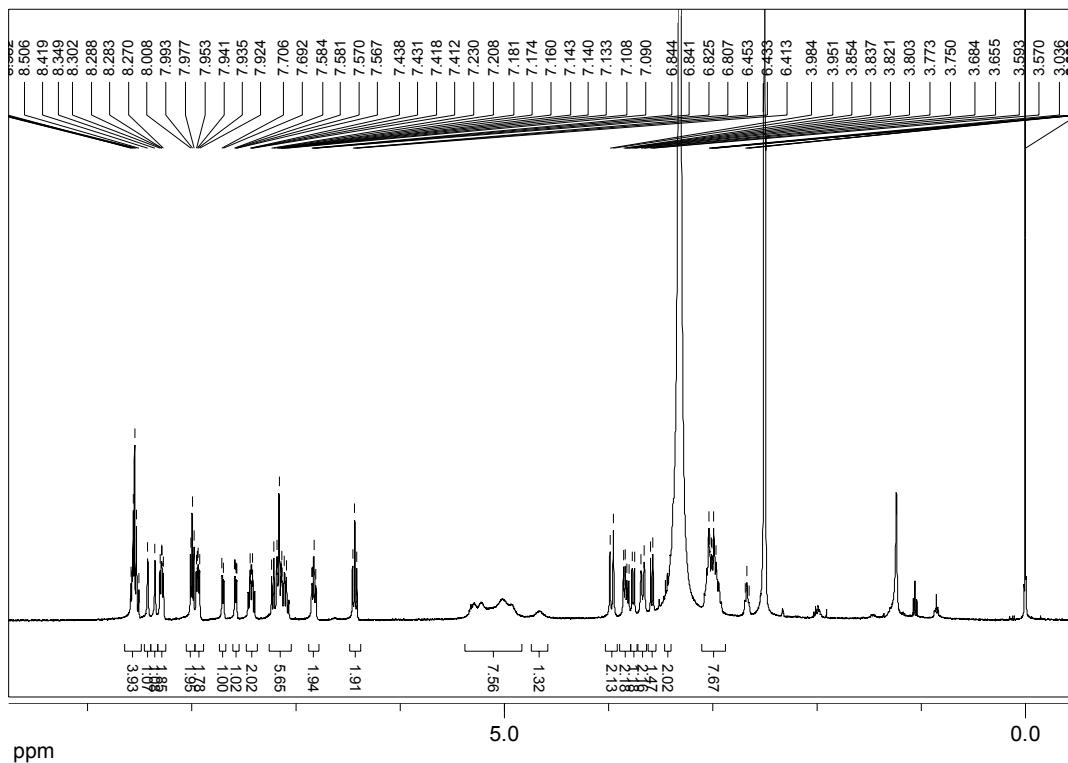


Figure S1. ¹H NMR spectrum of [Ir(pq)₂(bpy-sugar)]Cl in DMSO-d₆ at 25°C.

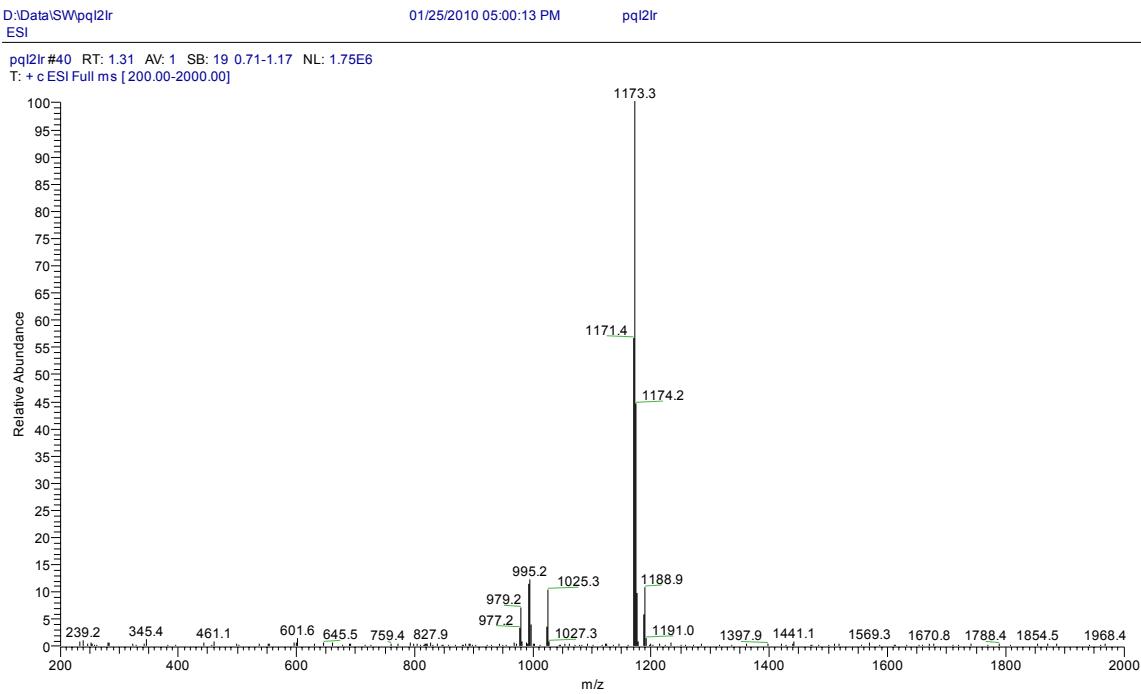


Figure S2. ESI-MS spectrum of [Ir(pq)₂(bpy-sugar)]Cl

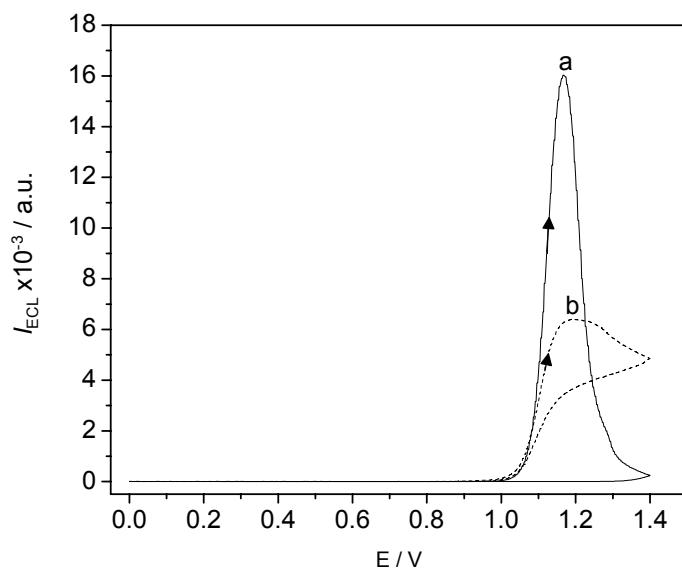


Fig. S3 ECL signals of the $[\text{Ir}(\text{pq})_2(\text{bpy-sugar})]^+$ (a) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (b) at a GC electrode in 0.15 M PBS (pH 7.5) containing 5 μM complex and 1 mM TPA. Scan rate: 0.1 Vs^{-1} .