Electronic Supplementary Information

A Novel Route Towards Water-Soluble Luminescent Iridium(III) Complexes via a Hydroxy-bridged Dinuclear Precursor

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PHOTOPHYSICAL STUDIES: Materials and methods

Spectrofluorimetric grade water was used for the photophysical investigations in solution without further purification. A Perkin Elmer Lambda 900 spectrophotometer was employed to obtain the UV/Vis absorption spectra. Steady-state emission spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The luminescence quantum yields were determined using the optical dilution method\[1\] using Ru(bpy)$_2$Cl$_2$ in air-equilibrated water solution as a reference standard ($\Phi = 0.028$).\[2\] Solutions were degassed by bubbling argon into quartz cells prior to measurements. Time-resolved measurements were performed using the time-correlated single-photon counting (TCSPC) on the Fluorolog-3 apparatus. A NanoLED pulses centered at 379 nm (FWHM 750 ps with 1 MHz repetition rate) was used as excitation source and fixed directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/mm). Data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The quality of the fit was assessed by minimizing the reduced $\chi^2$ function. The experimental uncertainties were 1 nm on the band maximum for the absorption and luminescence spectra, 10% on the molar extinction coefficient, 20% on the emission quantum yields and 5% on the lifetime values.
**Figure S1.** Absorption spectra of complexes $[(ppy)_2lr(bpy)](EtO)$ (1) and $[(ppy)_2lr(bpy)](OH)$ (2) in deaerated water solution.

**Figure S2.** Absorption spectra of complexes $[(ppy)_2lr(bpy)](OH)$ (2), $[(ppy)_2lr(bpy)](CH_3CH_2OCH_2CO_2)$ (3), $[(ppy)_2lr(bpy)](CH_3OCH_2CO_2)$ (4) in deaerated water solution ($C = 5.0 \times 10^{-6}$M).
Figure S3. Life time decay (τ, ns) and luminescence quantum yield (φ, %) of the exited state of the cation [(ppy)$_2$Ir(bpy)]$^+$ with increase of solvent polarity

*Note: Both data from our work and reported literature data$^{[3-5]}$ have been taken into account. The values of relative polarity have been normalised, taken from Christian Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH Publishers, 3rd ed., 2003.
Table S1. Photophysical data of complex 3 in deaerated water solution at various concentrations

<table>
<thead>
<tr>
<th>Complex</th>
<th>Concentration (mol.L⁻¹)</th>
<th>Emission, λ_{max}/nm</th>
<th>Lifetime, t/ns(α%)</th>
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<tbody>
<tr>
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<tr>
<td>5.0 x 10⁻⁴</td>
<td></td>
<td>606</td>
<td>40.9 (91.9) 531.0 (8.1)</td>
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<tr>
<td>1.3 x 10⁻⁴</td>
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<td>593</td>
<td>39.4 (81.57), 444.7 (18.43)</td>
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<tr>
<td>3</td>
<td>1.3 x 10⁻⁴</td>
<td>592</td>
<td>33.9 (60.72), 77.2 (34.44), 275.0 (4.84)</td>
</tr>
<tr>
<td></td>
<td>1.2 x 10⁻³</td>
<td>590</td>
<td>30.2 (47.27), 83.5 (45.85), 277.8 (6.87)</td>
</tr>
<tr>
<td></td>
<td>4 x 10⁻² (gel phase)</td>
<td>580</td>
<td>28.5 (17.2), 115.9 (55.0), 336.4 (27.8)</td>
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