Antagonist Effects Leading to Turn-on Electrochemiluminescence in Thermoresponsive Hydrogel Films

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A. Additional figures

Figure S1. Electrodeposition of a pNIPAM-Ru hydrogel film by cyclic voltammetry. Electrochemically assisted free radical polymerization was performed in a degassed solution containing 70 mM pNIPAM, 0.14 mM Ru(bpy)$_3$ monomer, 1.5 mM K$_2$S$_2$O$_8$, 1.75 mM BIS and
0.2 M KNO₃. The potential was scanned 60 times at a scan rate of 100 mV s⁻¹ between -0.35 and -0.9 V vs. Ag/AgCl. The arrow indicates the increasing scan number.

Figure S2. Scanning electron microscopy image of lyophilized hydrogel films on the GC electrode.

Figure S3. Voltammetric and ECL signals of a pNIPAM-modified GC electrodes recorded in a 100 mM PBS (pH7.4) solution containing 0.5 mM Ru(bpy)₃²⁺ and 100 mM TPA at 25°C (red curve) and at 40°C (blue curve). The film were prepared as in Figure S1 but without Ru(bpy)₃ monomer in the electrodeposition solution.
Figure S4. ECL spectra of the pNIPAM-Ru hydrogel film in the swollen state at 25°C (blue curve) and in the collapsed state at 40°C (red curve). Comparison with the photoluminescent spectrum (black curve) of the 10 µM Ru(bpy)$_3^{2+}$ complex in aqueous solution at 25°C. ECL spectra were acquired in 100 mM PBS solution (pH 7.4) containing 100 mM TPA during cyclic voltammetry experiments. The potential was scanned from 0.2 V to 1.45 V at a scan rate of 50 mV s$^{-1}$.

Figure S5. Voltammetric (a) and ECL signal (b) of a GC electrode modified with a pNIPAM-Ru film in a 100 mM PBS solution containing 20 mM DBAE at 25°C (blue curve) and at 40°C (red curve). Scan rate: 100 mV s$^{-1}$. 
Table S1. Variations of the faradaic charge ratio and of the ECL signal ratio for different coreactants between 25°C (swollen state) and 40°C (collapsed state).

<table>
<thead>
<tr>
<th>Coreactant(a)</th>
<th>Faradaic charge at 25°C Q²⁵°C (µC)</th>
<th>Faradaic charge at 40°C Q°⁴⁰°C (µC)</th>
<th>ECL signal at 25°C 𝐼_{ECL}²⁵°C (10³ a.u.)</th>
<th>ECL signal at 40°C 𝐼_{ECL}°⁴⁰°C (10³ a.u.)</th>
<th>Faradaic charge ratio Q°⁴⁰°C / Q²⁵°C</th>
<th>ECL signal ratio 𝐼_{ECL}°⁴⁰°C / 𝐼_{ECL}²⁵°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA</td>
<td>46±3</td>
<td>14.3±13</td>
<td>5±0.4</td>
<td>188±53</td>
<td>0.31±0.28</td>
<td>38±12</td>
</tr>
<tr>
<td>DBAE</td>
<td>39±2</td>
<td>13.7±3</td>
<td>1.7±0.07</td>
<td>67±3</td>
<td>0.31±0.1</td>
<td>40±1</td>
</tr>
<tr>
<td>Oxalate</td>
<td>13.7±0.4</td>
<td>17.5±0.7</td>
<td>2.68±0.07</td>
<td>155±4</td>
<td>1.28±0.06</td>
<td>58±3</td>
</tr>
</tbody>
</table>

B. Experimental section

Chemicals.

All the reagents were purchased from Sigma-Aldrich unless otherwise noted. N-isopropylacrylamide (NIPAM) was recrystallized from hexane (ICS) and dried under vacuum prior to use. The cross-linker N,N’-methylenebis(acrylamide) (BIS) and the initiator potassium persulfate were used as received. Ruthenium(II) (4-vinyl-4’-methyl-2,2’-bipyridine)bis(2,2’-bipyridine)bis(hexafluorophosphate) [Ru(bpy) monomer] was synthesized according to the procedure described by Spiro et al.¹ The coreactants, n-tripropylamine (TPA), dibutylaminoethanol (DBAE) and sodium oxalate, were purchased from Sigma Aldrich. De-ionized water, obtained with a Milli-Q system, was used for all synthesis reactions, purification and solution preparation.

Preparation of electrodes modified with pNIPAM-Ru films

Glassy carbon (GC) electrodes were polished with wet alumina powder on a polishing cloth, and then washed ultrasonically with ethanol and water, respectively. In a typical process, the electrode was immersed in an aqueous solution containing 70 mM NIPAM, 1.75 mM BIS (2.5 mol % against NIPAM), 0.14 mM of Ru(bpy) monomer (0.2 mol % of Ru monomer against NIPAM), and 1.5 mM K₂S₂O₈ in 0.2 M KNO₃ solution. Prior to electrochemically assisted polymerization, the reaction solution was deoxygenated by bubbling nitrogen gas for 30 min at room temperature. The potential was applied by cycling between -0.35 and -1.35 V at 100 mV s⁻¹ for 60 cycles. After the polymerization, the electrodes modified with pNIPAM-Ru films were thoroughly washed with double-distilled water to remove the monomers and stored in ultrapure water.
Characterization of the hydrogel film

Scanning electron microscopy (SEM)

A flat glassy carbon plate was used as working electrode and modified using the same procedure as described on the macroscopic electrode. After rinsing with distilled water, it was immersed in a water bath and frozen rapidly in liquid nitrogen. After freeze drying, the electrode was sputtered with gold using a sputter-coater (Emitech K550X) and observed in SEM (Hitachi TM3000).

Electrochemical measurements

Differential pulse voltammetry (DPV) experiments were performed with a μ-Autolab Type III and PGSTAT30 electrochemical stations. The three-electrode system consisted in a glassy carbon (GC) electrode as a working electrode, Ag wire as a pseudo-reference and a platinum wire as a counter-electrode. The temperature of the sample was controlled using a thermostatically controlled cell compartment. The measurements were taken under equilibrium conditions after holding the sample for 15 min at the required temperature.

Electrochemiluminescence. ECL experiments were performed with a μ-Autolab Type III electrochemical station. ECL intensity was measured by using a Hamamatsu photomultiplier tube R4632. The signal was amplified by a Keithley Picoammeter before acquisition via the second input channel of the μ-Autolab. ECL spectra were recorded using a Princeton Instrument spectrograph Spectra pro 2300i under potential scanning between 0.2 and 1.45 V at a scan rate of 50 mV/s, in an aqueous solution containing the coreactant and the supporting electrolyte. The temperature of the sample was controlled using a thermostatically controlled cell compartment. The measurements were taken under equilibrium conditions after holding the sample for 15 min at each temperature.

C. References