

## Electronic Supplementary Information

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

Haidong Li, Milica Sentic, Valérie Ravaine\*, Neso Sojic\*

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A. Additional figures	1
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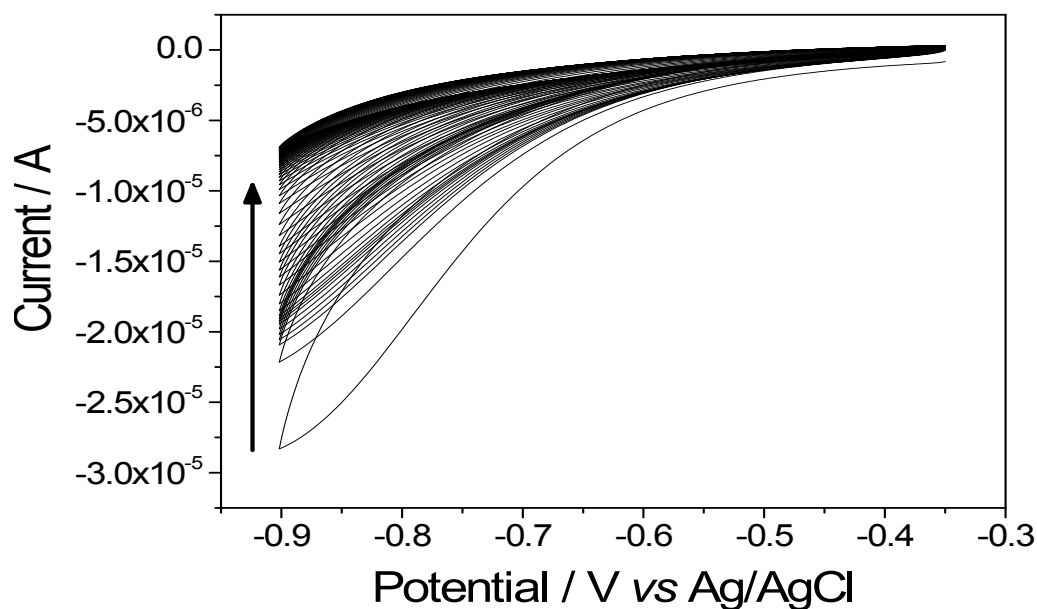


Figure S1. Electrodeposition of a pNIPAM-Ru hydrogel film by cyclic voltammetry. Electrochemically assisted free radical polymerization was performed in a degassed solution containing 70 mM pNIPAM, 0.14 mM Ru(bpy)<sub>3</sub> monomer, 1.5 mM K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1.75 mM BIS and

0.2 M  $\text{KNO}_3$ . The potential was scanned 60 times at a scan rate of  $100 \text{ mV s}^{-1}$  between  $-0.35$  and  $-0.9 \text{ V vs. Ag/AgCl}$ . The arrow indicates the increasing scan number.

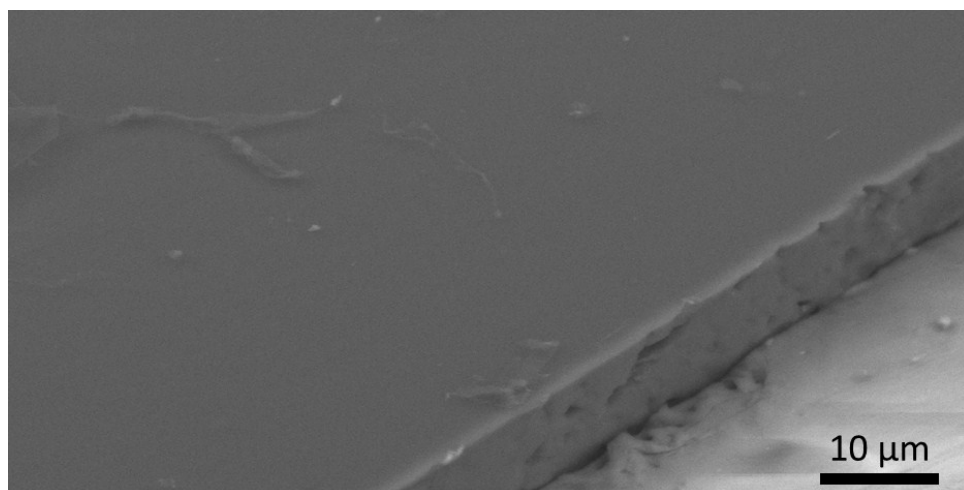


Figure S2. Scanning electron microscopy image of lyophilized hydrogel films on the GC electrode.

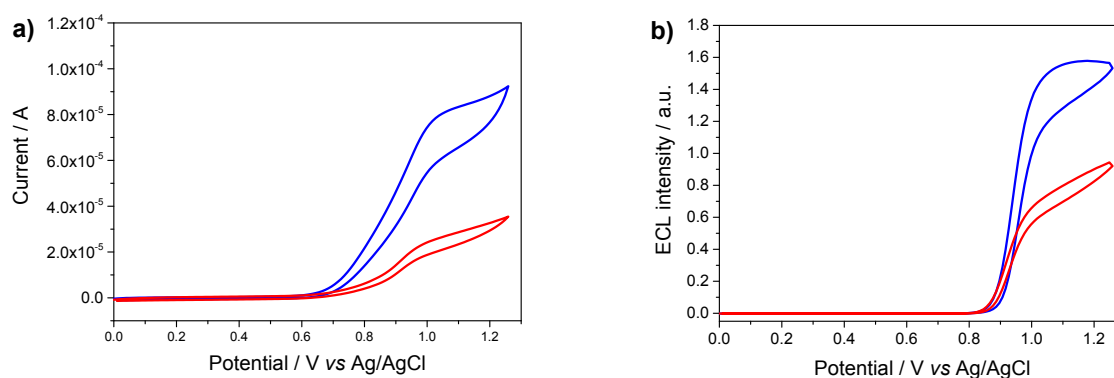


Figure S3. Voltammetric and ECL signals of a pNIPAM-modified GC electrodes recorded in a 100 mM PBS (pH7.4) solution containing  $0.5 \text{ mM Ru}(\text{bpy})_3^{2+}$  and 100 mM TPA at  $25^\circ\text{C}$  (red curve) and at  $40^\circ\text{C}$  (blue curve). The film were prepared as in Figure S1 but without  $\text{Ru}(\text{bpy})_3$  monomer in the electrodeposition solution.

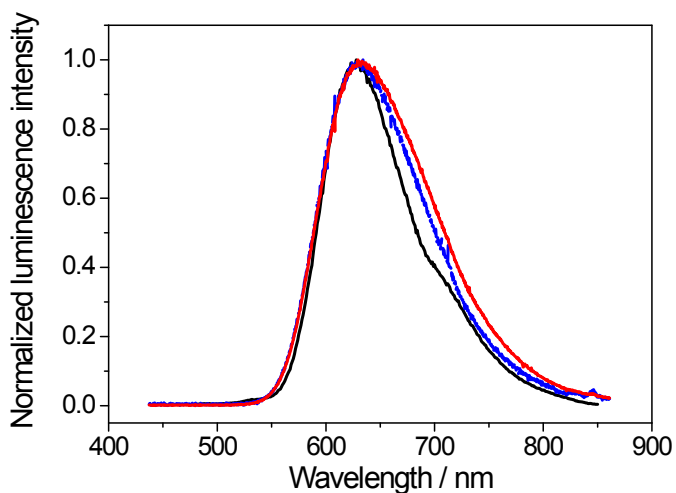


Figure S4. ECL spectra of the pNIPAM-Ru hydrogel film in the swollen state at 25°C (blue curve) and in the collapsed state at 40°C (red curve). Comparison with the photoluminescent spectrum (black curve) of the 10  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  complex in aqueous solution at 25°C. ECL 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  $\text{mV s}^{-1}$ .

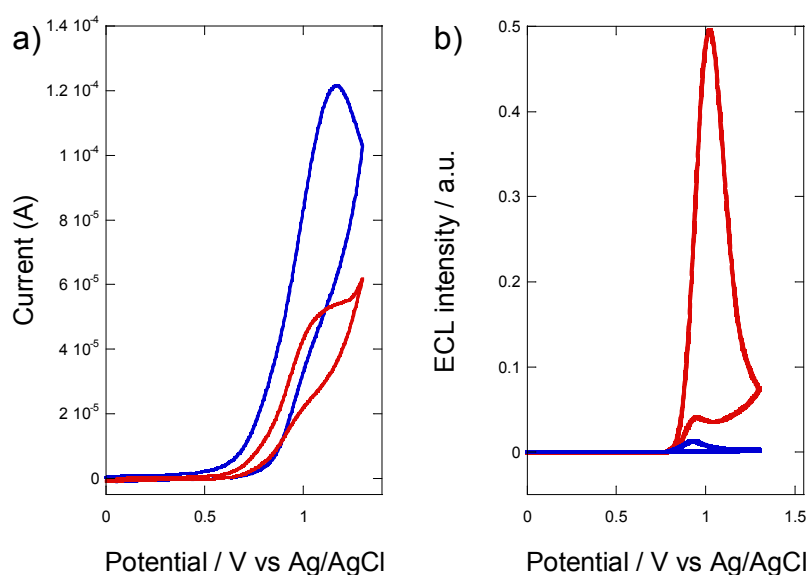


Figure S5. Voltammetric (a) and ECL signal (b) of a GC electrode modified with a pNIPAM-Ru film in a 100 mM PBS solution containing 20 mM DBAE at 25°C (blue curve) and at 40°C (red curve). Scan rate: 100  $\text{mV s}^{-1}$ .

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).

Coreactant <sup>(a)</sup>	Faradaic charge at 25°C $Q^{25^\circ\text{C}}$ ( $\mu\text{C}$ )	Faradaic charge at 40°C $Q^{40^\circ\text{C}}$ ( $\mu\text{C}$ )	ECL signal at 25°C $I_{ECL}^{25^\circ\text{C}}$ ( $10^3$ a.u.)	ECL signal at 40°C $I_{ECL}^{40^\circ\text{C}}$ ( $10^3$ a.u.)	Faradaic charge ratio $Q^{40^\circ\text{C}} / Q^{25^\circ\text{C}}$	ECL signal ratio $I_{ECL}^{40^\circ\text{C}} / I_{ECL}^{25^\circ\text{C}}$
TPA	46±3	14.3±13	5±0.4	188±53	0.31±0.28	38±12
DBAE	39±2	13.7±3	1.7±0.07	67±3	0.31±0.1	40±1
Oxalate	13.7±0.4	17.5±0.7	2.68±0.07	155±4	1.28±0.06	58±3

## 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.<sup>1</sup> 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  $\text{K}_2\text{S}_2\text{O}_8$  in 0.2 M  $\text{KNO}_3$  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  $\text{s}^{-1}$  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  $\mu$ -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  $\mu$ -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  $\mu$ -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

- 1 P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 5543-5549.