Endogenous and exogenous wireless multimodal light-emitting chemical devices

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Experimental

Tris(2,2'-bipyridil) dichlororuthenium (II) hexahydrate ($Ru(bpy)_3Cl_2$, Aldrich, 97%), tri-n-propylamine (TPrA, Aldrich, ≥ 98%), 8-Amino-5-chloro-7-phenylpyrido[3,4-d]pyridazine-1,4-(2H,3H)dione Sodium Salt (L012, FUJIFILM Wako), sulfuric acid (H2SO4, J. T. Baker, 95%-97%), hydrogen peroxide (H_2O_2, Alfa Aesar, 27%), potassium peroxodisulfate (K2S2O8, Fluka, > 98%), disodium hydrogen phosphate heptahydrate ($Na_2HPO_4{\cdot}7H_2O$, Aldrich, 98%-102.0%), and sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$, Aldrich, ≥ 99.5%), agar silver paste (Agar scientific Ltd.), porous glass CoralPor® (BASi®), green light-emitting diodes (LED, 0603 SMD diode, OSRAM Opto Semiconductors, 1.70 mm × 0.8 mm), Au wire (ø = 0.25 mm, Alfa Aesar, 99.9%), stainless steel wire (Fe/Cr18/Ni10/Mo3, ø = 0.10 mm, GoodFellow), Mg wire (ø = 0.5 mm) and Pt wire (ø = 0.25 mm, 99.9%, AlfaAesar) were used as received. All solutions were prepared with deionized water (MilliQ Direct-Q, resistivity of 18.2 MΩ.cm at 25°C). All the bipolar devices were assembled as follows: at first two metal wires (l ≈ 1 cm) and the LED were immobilized at the bottom of the bipolar cell. Afterwards, the electric connection was established at the anode and cathode of the LED by using a small volume of agar silver paint, followed by an insulating layer to avoid short-circuiting. The total length of all the bipolar electrodes is around 2.1 cm). For the exogenous (non-spontaneous) bipolar electrochemical system, two different hybrid BPEs were designed; an Au-LED-Au and a Fe-LED-Fe (Scheme 1a and b). The bipolar electrochemical measurements were carried out by applying different electric fields between two graphite feeder electrodes, positioned at the extremities of the bipolar cell at a distance of 5 cm. For the endogenous (spontaneous) bipolar electrochemical systems, two different bipolar electrodes were designed; a Pt-LED-Mg and a Fe-LED-Mg (Scheme 1c and d). Light emission was monitored by using a CCD camera (CANON EOS 70D, Objective Canon Macro Lens 100 mm 1:2.8) and the images were processed with Image J software. Potentiodynamic measurements were performed using a three-electrode cell composed of an Au or a Fe wire acting as a working electrode and a Pt wire and an Ag/AgCl as counter and reference electrodes, respectively. All measurements were carried out with a Hamamatsu photomultiplier tube (PMT) R5070A and a µ-Autolab type III potentiostat connected to a personal computer. The voltage of the PMT was controlled at 750 V.

Results and discussion

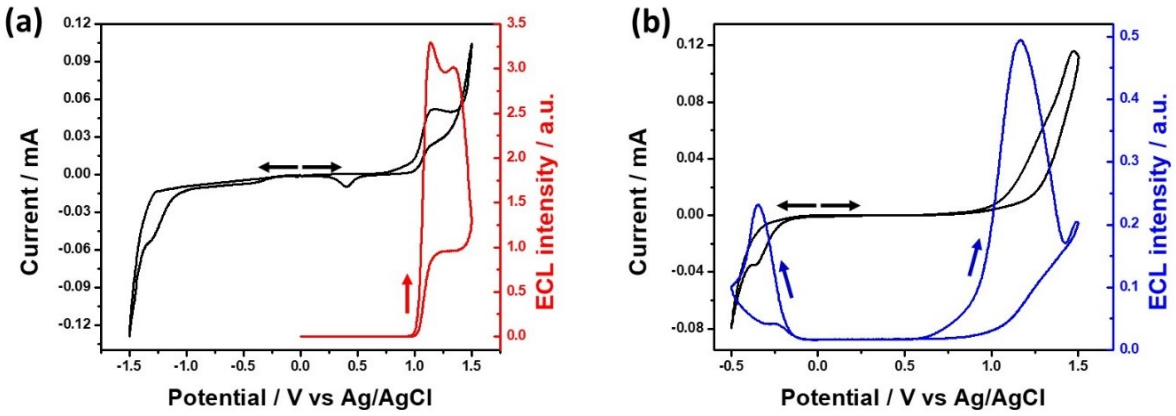

Figure S1. Simultaneous electrochemical (left axis) and ECL (right axis) responses of (a) a 0.1 M PBS (pH 7.4), 1 mM $Ru(bpy)_3^{2+}$, 100 mM TPrA solution using an Au disk working electrode (A≈ 0.05 mm^2) and (b) a 0.1 M PBS (pH 7.4), 1 mM L012, 100 mM H_2O_2 solution using a Fe disk working electrode (A≈ 0.008 mm^2). Scan rate: 100 mV s^{-1}.

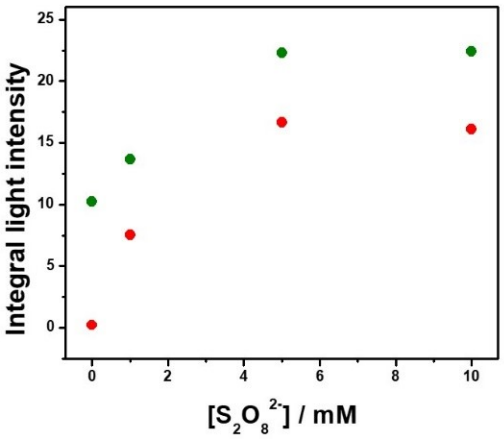

Figure S2. Integral of the light intensity as a function of the co-reactant $S_2O_8^{2-}$ concentration obtained for a Pt-LED-Mg BPE in a 0.1 M PBS (pH 7.4), 1 mM $Ru(bpy)_3^{2+}$, 10 mM H_2SO_4 solution. The green dots symbolize the light intensity produced by the LED, whereas the red dots indicate the ECL emission of $Ru(bpy)_3^{2+}$.

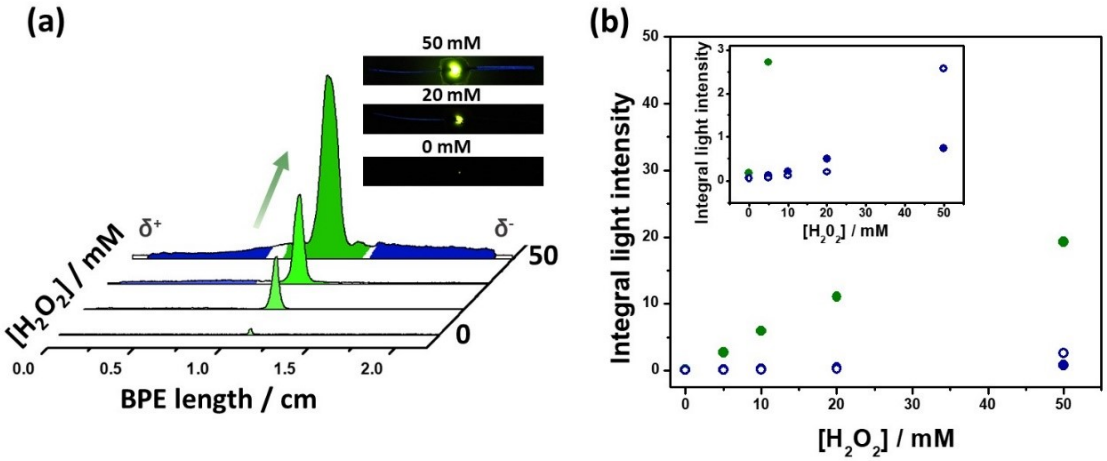

Figure S3. (a) 3D light intensity profiles as a function of the co-reactant H_2O_2 concentration (indicated in the figure) obtained with a Fe-LED-Mg device in a 0.1 M PBS (pH 7.4), 1 mM L012 solution. Inset: optical pictures of the corresponding endogenous multimodal light-emitting devices at different co-reactant H_2O_2 concentrations (indicated in the figure). (b) Integral of the light intensity as a function of the co-reactant H_2O_2 concentration obtained with a Fe-LED-Mg BPE in a 0.1 M PBS (pH 7.4), 1 mM L012 solution. The blue plain and empty dots stand for the ECL at the cathodic and anodic extremities of the BPE, respectively.

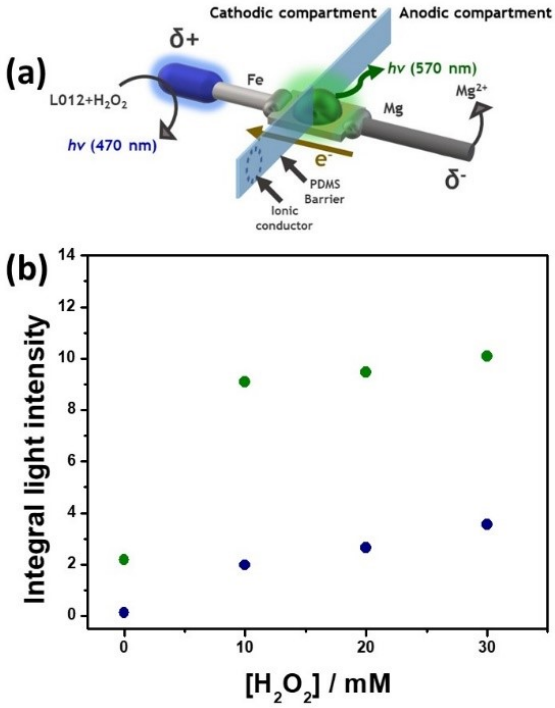

Figure S4. (a) Schematic illustration of the divided light-emitting bipolar electrode used for the endogenous bipolar electrochemistry approach, with a representation of the associated chemical reactions, the electron flux, the physical separation, the ionic conductor (dotted lines) and the color of the resulting light emissions. (b) Integral of the light intensity as a function of the co-reactant concentration (indicated in the plot) obtained for a divided Fe-LED-Mg device in a 0.1 M PBS (pH 7.4) solution, in the presence of L012 (1 mM) and H_2SO_4 (10 mM) in the cathodic and anodic compartments, respectively. The green dots symbolize the light intensity produced by the LED, whereas the blue dots indicate the ECL emission of L012, respectively.

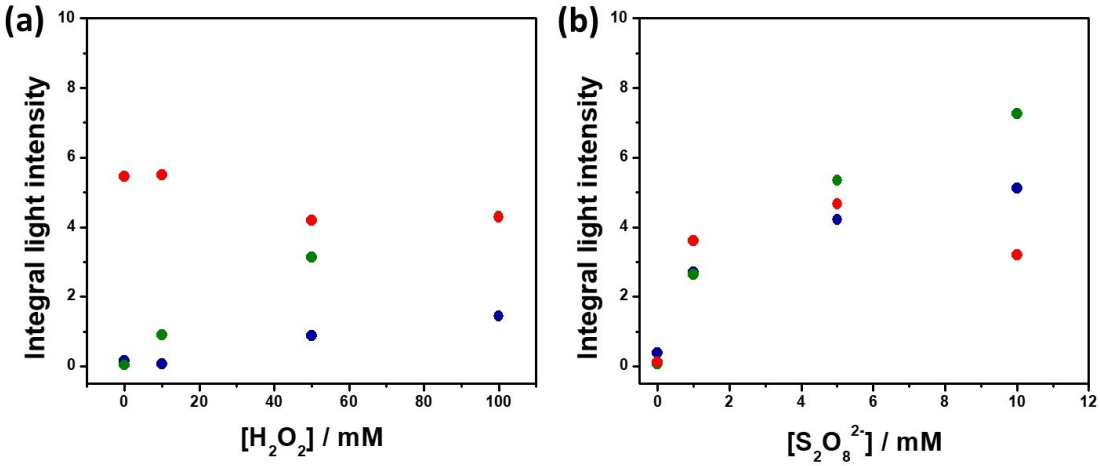

Figure S5. Integral of the light intensity as a function of the co-reactant concentration (indicated in the plot) obtained for a divided Fe-LED-Mg device in a 0.1 M PBS (pH 7.4) solution, in the presence of (a) L012 (1 mM) at the cathodic side and $Ru(bpy)_3^{2+}$ (1 mM), H_2SO_4 (10 mM) and $S_2O_8^{2-}$ (20 mM) in the anodic part, and (b) L012 (1 mM) and H_2O_2 (100 mM) in the cathodic compartment and $Ru(bpy)_3^{2+}$ (1 mM), H_2SO_4 (10 mM) on the anodic side. The green dots symbolize the light intensity produced by the LED, whereas the red and blue dots indicate the ECL emission of $Ru(bpy)_3^{2+}$ and L012, respectively.