

Supporting information

Experimental details

The experimental setup for ECL measurements is shown in Figure 1(C), which consists a BPCL Ultra-Weak Luminescence Analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) and a model VMP3 Multichannel Potentiostats and Power Boosters (Princeton Applied Research, USA). A homemade multiplex was used for the independent and simultaneous control the addressing working electrodes. All experiments performed using a Pt quasi-reference electrode. The counter electrode was a platinum wire. The microelectrode array chip was placed directly at the top of the photomultiplier tube (PMT) and was fixed in a dark detection chamber. The PMT was operated at -850 V. The entire ECL measurement setup was placed inside of a light-tight box.

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ was obtained from Sigma Chemical Company and used without further purification, which had been dissolved in acetonitrile solution worked as ECL reagent. 0.2 mol/L tetra-*n*-butyl-ammonium tetrafluoroborate (TBABF_4) acts as the supporting electrolyte. All solutions were deaerated before and between measurements with N_2 for at least 10 min.