Supporting Information

Glucose-Powered Antimicrobial System Using Organic/Inorganic Assembled Network Materials

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Experimental Section

Materials and methods

All chemicals were purchased from Acros, Aldrich Chemical Company or Alfa-Aesar and used as received. All organic solvents were purchased from Beijing Chemical Works and used as received. Compound OPV was synthesized according to the previous procedure in the literature (H. Yuan, H. Chong, B. Wang, C. Zhu, L. Liu, Q. Yang, F. Lv, S. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 13184-13187). *Candida albicans* (*C. albicans*) was obtained from China General Microbiological Culture Collection Center. The Amp^r *Escherichia coli* (*E. coli*)

was purchased from Beijing Bio-Med technology Development Co., Ltd. The enzyme cascade activity was measured on a JASCO V-550 spectrophotometer. Luminescence spectra were measured on a Hitachi F-4500 fluorometer. Sizes of the particles were measured on a Nano ZS (ZEN 360) system. Bright-field and fluorescence images were taken with a confocal laser scanning microscope (FV1200-IX81, Olympus, Japan). SEM images were recorded on a Hitachi S-4800 scanning electron microscope. The images of plate counting were taken by a Bio-Rad Molecular Imager ChemiDoc XRS system.

Preparation of 5'-AMP/Gd^{3+} and 5'-AMP/Gd^{3+}-(GOx+HRP) network materials

To 1 mL of 10 mM 5'-AMP disodium salt aqueous solution in HEPES buffer (0.1 M, pH 7.4), was added 1 mL of 100 mM $GdCl_3$ aqueous solution at room temperature. After vortex-mixing for 2 h, the formed precipitates were collected by centrifugation (13000 rpm × 5 min). The obtained material was washed with pure water (2 mL) and collected by centrifugation (13000 rpm × 5 min). The washing procedure was repeated once again. The precipitates were suspended in 2 mL of 0.1 M HEPES buffer and the 5'-AMP/Gd^{3+}network materials were obtained. The encapsulations of GOx and HRP within 5'-AMP/Gd^{3+} were performed by mixing 1 mL of 10 mM aqueous 5'-AMP disodium salt in 0.1 M HEPES buffer, 200 μL of 10 mg/mL GOx in phosphate buffer saline (PBS, 10 mM, pH 7.4), 100 μL of 10 mg/mL HRP in PBS and 1 mL of 100 mM $GdCl_3$ aqueous solution. The following steps are the same as the preparation of 5'-AMP/Gd^{3+}network materials. The obtained material suspensions were reserved at 4°C for use.

Enzyme cascade reaction activity assay

To 1.7 mL of PBS solution, 20 μL of 4 mM ABTS aqueous solution, 70 μL of 1 M glucose in PBS and 10 μL of 5'-AMP/Gd^{3+}-(GOx+HRP) suspension were added. Time-dependent absorbance changes at 414 nm were recorded after 30 s. For the case of control group, 5'-AMP/Gd^{3+}-(GOx+HRP) suspension was replaced by 5'-AMP/Gd^{3+} suspension. PBS was used as the reference and the measurements lasted 10 min.

Spectral measurements for 5'-AMP/Gd^{3+}-(GOx+HRP)-based BRET to OPV

To 800 μL of 1 M glucose solution in PBS, 20 μL of 1 mg/mL enhancer (PC_3SO_3Na), 100 μL of 20 mM luminol and 40 μL of PBS/OPV (1 mM) were added. After vortex-mixing for 5 s, 40 μL of 5'-AMP/Gd^{3+}-(GOx+HRP) suspension was added to the mixture. The luminescence spectra were measured and the luminescence intensity changes at 425 nm and 550 nm were recorded.

Preparation of microbe suspension

A single colony of *C. albicans* on a solid Yeast-extract Tryptone Dextrose (YTD) agar plate was transferred to 6 mL of liquid YPD culture medium and grown at 30°C. *C. albicans* was harvested by centrifuging (7100 rpm for 1 min) and washing with PBS for three times. The supernatant was discarded and the remaining *C. albicans* was resuspended in PBS, and diluted to an optical density of 1.0 at 600 nm (OD_{600}=1.0). As for Amp^r *E. coli*, except that the culture medium and temperature were replaced by Luria Broth (LB, supplemented with100 $mg{\cdot}mL^{-1}$ ampicillin) and 37°C respectively, other operations are totally the same as

that of *C. albicans*.

Scanning electron microscope (SEM) characterization

After the treatment described in antimicrobial experiments, *C. albicans*/*E. coli* were centrifuged (10000 rpm, 2 min) and the supernatant was removed, and then the pellets were suspended and fixed with 100 μL glutaraldehyde (0.1%) in PBS at room temperature for 30 min. 2 μL of suspension were dropped on clean silicon slices followed by naturally drying in the air. Immediately the specimens became dried, 0.1% glutaraldehyde was added for further fixation for 1 h and then 0.5% glutaraldehyde for another 1-2 h at the room temperature. Next, the specimens were washed with sterile water for 2 times and then were dehydrated by addition of ethanol in a graded series (40%, 70%, 90% and 100% for 6 min, respectively) followed by lyophilization. Finally, the specimens were coated with platinum before characterization in SEM.

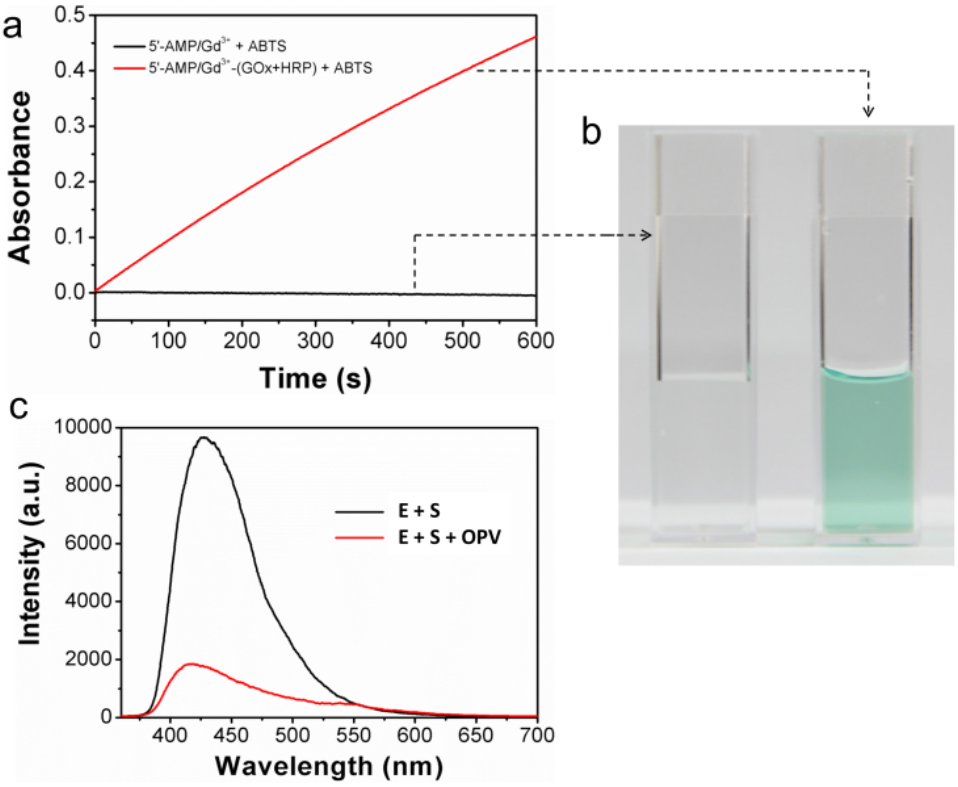
Antimicrobial experiment

E. coli cells were firstly incubated with OPV (2 μM) at 37°C for 15 min in the dark in PBS containing 0.6 M glucose. Then 20 μL of 5'-AMP/Gd^{3+}-(GOx+HRP) suspension and substrate (0.02 mg/mL PC_3SO_3Na and 2 mM luminol) were added and then allowed vortex-mixing for 5 min in the dark. Finally, the *E. coli* suspensions were serially diluted 1×10^4 fold with PBS and a 100 μL portion of the diluted was spread on the solid LB (supplemented with 100 $mg \cdot mL^{-1}$ ampicillin) agar plate. The colonies formed after 24 h incubation at 37°C were counted. The diameter of the solid agar plates was 90 mm. The inhibition ratio (IR) was

calculated according to the following equation:

$$IR = \frac{C_0 - C}{C_0} \times 100\%$$

Where C is the cfu of the experimental groups and C_0 is the cfu of the control group without incubation with neither OPV nor the 5'-AMP/Gd^{3+}-(GOx+HRP) materials and substrates.



FigureS1.(a) Time-dependent absorbance changes of ABTS at 414 nm in the presence of 5'-AMP/Gd^{3+} and 5'-AMP/Gd^{3+}-(GOx+HRP) composites. (b) A photograph of the mixture of glucose and ABTS in the presence of 5'-AMP/Gd^{3+} and 5'-AMP/Gd^{3+}-(GOx+HRP) composites. [ABTS] = 44 μM, [glucose] = 39 μM. (c)The luminol luminescence spectra of 5'-AMP/Gd^{3+}-(GOx+HRP) composite in the presence of glucose and luminol substrates (E+S) before and after addition of OPV. [glucose] = 0.8 M, [luminol] = 2 mM, [OPV] = 40 μM.

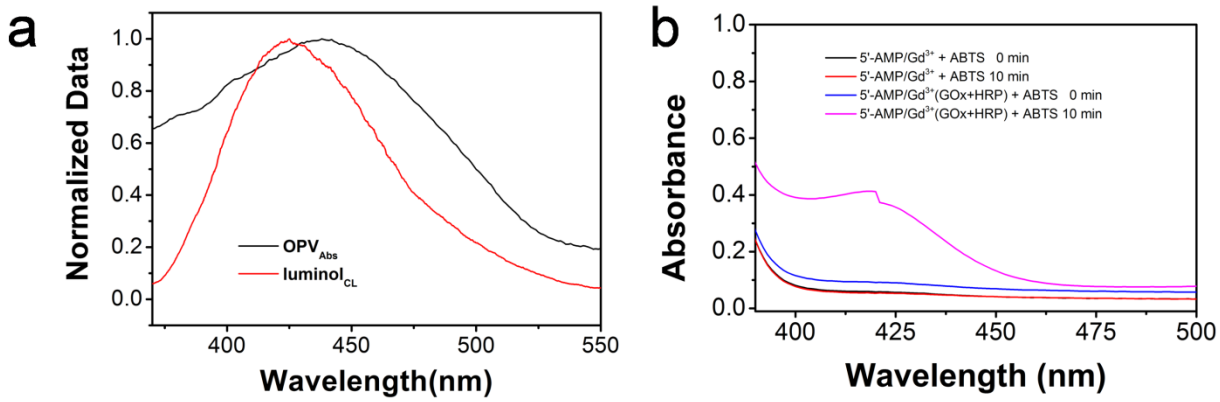


Figure S2. (a) Normalized absorption spectrum of OPV and luminescence spectrum of luminol. (b) The absorption spectra of ABTS in the presence of 5'-AMP/Gd^{3+} and 5'-AMP/Gd^{3+}-(GOx+HRP) composites at the beginning and 10 min, respectively.