Supporting Information

Electrochemiluminescence and conjugated polymer based photosynthesis system for regulating the photoreaction of cyanobacterium

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Experimental

Materials and instruments

All chemicals and solvents used in the experiments were bought from Acros, Sigma-Aldrich Chemical Company, or Beijing Chemical Works, and used as received. Indium tin oxide (ITO)-coated glass slides (resistance, 15~20 ohms/square) were purchased from South China Xiangcheng Technology Co. UV-Vis absorption spectra were measured by Thermo Scientific Evolution 201 spectrophotometer. *Synechococcus* sp. PCC7942 was purchased from Freshwater Algae Culture Collection. Fluorescence spectra were measured by Hitachi F-4500 fluorometer equipped with a xenon lamp excitation source. Transmission electron microscopy were measured by JEM-F200, JEOL. Dynamic light scattering was tested by Nano ZS90 (Malvern, UK). Cyclic voltammetry and electrochemiluminescence experiments were carried out with Shanghai Chenhua electrochemical workstation. The ECL intensity was measured by MPI-EII electrochemiluminescence (ECL) workstation (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China). Chlorophyll fluorescence parameters were carried out with Handy PEA chlorophyll fluorimeter and FMS-2 pulse modulated fluorimeter (Hansatech, United Kingdom). Amplite™ fluorimetric NADP/NADPH ratio assay kit was purchased from AAT Bioquest®. Enhanced ATP assay kit was bought from Beyotime Biotechnoloty. Confocal laser scanning microscope (CLSM) images were carried out with a confocal laser scanning microscope (Olympus FV 1200-BX61, Japan).

Synechococcus sp. PCC7942 culture and quantification

Synechococcus sp. PCC7942 cells were cultured with sterile BG11 medium in conical flasks at 25℃ in an illumination incubator, with a continuous irradiance of 1500 lux of white light on a cycle of 12 h of light and 12 h of dark. The conical flasks were shook manually 3 times per day. The concentration of Syne was determined by the optical density at 680 nm (OD_{680}).

ECL intensity measurements of luminol system

The ECL experiments were conducted with three electrodes system, which comprised of a platinum wire electrode as the auxiliary electrode, a glassy carbon electrode (GCE)

as working electrode and an Ag/AgCl electrode as reference electrode. The detection cell contained different concentrations of luminol (0.1, 0.2, 0.4 and 0.8 mM) and H_2O_2 (1 mM). The photomultiplier bias was set to 600 V. The ECL was captured between 0.2 and 0.6 V at 100 mV s^{-1}.

CV experiments of luminol system

The CV experiments were conducted with a three-electrode system with a platinum wire electrode as the auxiliary electrode, a glassy carbon electrode (GCE) as the working electrode and an Ag/AgCl electrode as the reference electrode to conduct. The detection cell contained H_2O_2 (1 mM) and luminol (0.4 mM). The scanning speeds were 0.1 V/s, and the scanning range was 0.2-0.6 V.

Chlorophyll fluorescence parameters measurements

The chlorophyll fluorescence parameters of *Syne* and *Syne*/PFBT-NPs were determined with Handy PEA chlorophyll fluorometer and FMS-2 pulse-modulated fluorometer. *Syne* or *Syne*/PFBT-NPs suspensions were added into the sample bottles. After the dark treated for 30 min, FMS-2 and Handy PEA fluorometer measured the chlorophyll fluorescence parameters.

Measurement of DCPIP

DCPIP (100 μM) was added into the suspensions of *Syne* (OD_{680}=1). After irradiated with ECL systems under different times (0, 30, 60, 90 min), the absorbance of the solutions at 600 nm was measured.

Preparation of PFBT nanoparticles (PFBT-NPs)

PFBT-NPs were prepared with nanoprecipitation method. 5 mL of THF solution containing conjugated polymer PFBT (2 mg mL^{-1}) and PSMA (2 mg mL^{-1}) were rapidly added into 20 mL of ultrapure water and sonicated for 2 min. Then, filtering through 0.22 μm filter. Finally, obtaining the product after 30 min of spin evaporation treatment.

Measurement of ATP synthesis

In the experimental group, *Syne* suspension (OD_{680}=1) mixed thoroughly with the luminol (0.1, 0.2, 0.4, 0.8 mM), and the PFBT-NPs (2 μg/mL). Controls were ECL systems with *Syne* suspension, without PFBT-NPs. All suspensions were divided into three groups. After 120 min of ECL irradiation, extracting the ATP from the

suspensions according to the instructions of the kit. Then measuring the ATP content by ATP bioluminescence detection kit (Beyotime Biotechnology).

Measurement of NADPH and $NADP^+$ synthesis

Syne suspension (OD_{680}=1) mixed thoroughly with the luminol (0.1, 0.2, 0.4, 0.8 mM), and the PFBT-NPs (2 μg/mL). Then, centrifugating at 3000 rpm for 3 min and resuspending in 400 μL of lysate. After 30min of ice bath, centrifugating at 12000rpm for 5min and adding to a black 96-well plate. Detecting the NADPH and $NADP^+$ by AmpliteTM fluorescent NADP/NADPH ratio assay kit.

Confocal laser scanning microscopy characterization

After 1 mL *Syne* (OD_{680}=1) was incubated with 2 μg/mL PFBT-NPs, *Syne* was centrifuged at 7200 rpm for 3 min and washed with ultrapure water twice to get the final pellet, which was resuspended in 50 μL of ultrapure water. Then, 3 μL of concentrated liquor was added to a thin glass for imaging. The laser to excite PFBT-NPs and *Syne* was 488 nm.

Oxygen evolving activity measurements

Oxygen evolving activities of *Syne* and *Syne*/PFBT-NPs were measured with a Clark-type oxygen electrode in BG-11 medium. *Syne* suspension was collected by centrifuging at 7200 rpm for 3 min. The supernatant was discarded, and the remaining *Syne* were resuspended in fresh BG-11 medium to an optical density of 2.0 at 680 nm (OD_{680}=2.0). Cell resuspensions (2 mL) were incubated with PFBT-NPs (2 μm/mL) at room temperature for 15 min. As control, 2 mL cell resuspensions were added to equal volume of ultrapure water. The oxygen electrode chamber was loaded with samples, and then argon was passed into the solution for deoxygenation. Finally, the amount of oxygen evolving was recorded under uniform illumination intensity (1400 μmol m^{-2} s^{-1}) at 25℃.

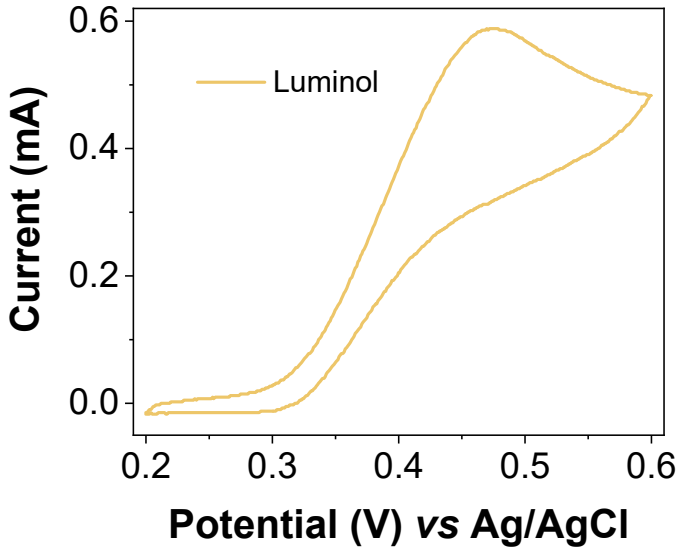

Figure S1. The cyclic voltammetry curve of luminol.

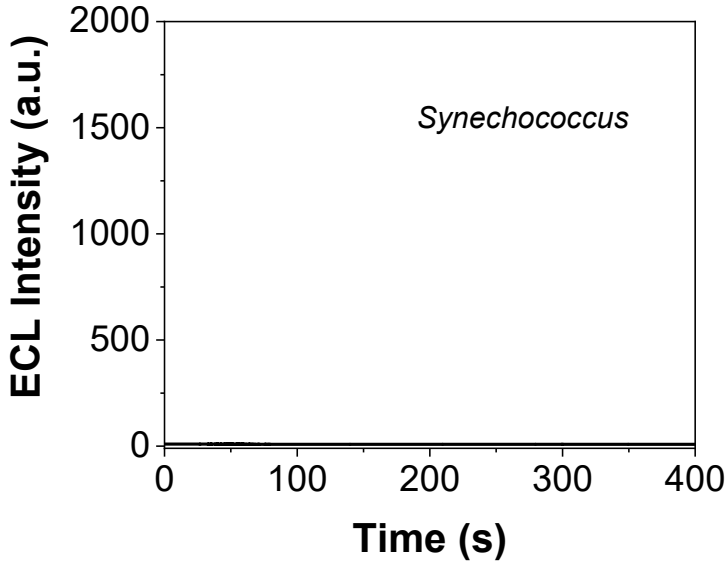

Figure S2. The ECL intensity curve of *Syne*.

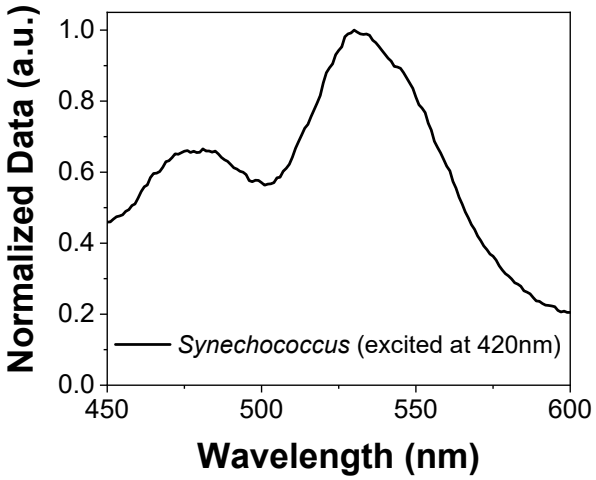

Figure S3. Fluorescence spectra of *Syne* excited at 420 nm.

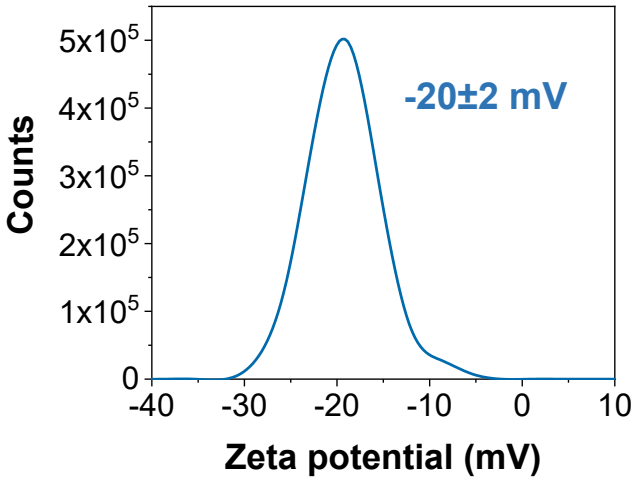

Figure S4. The zeta potential of PFBT-NPs.

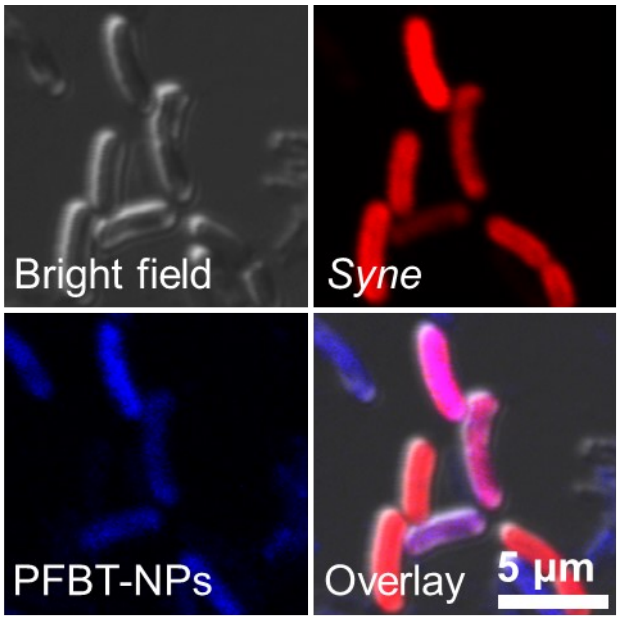

Figure S5. CLSM images of *Syne*/PFBT-NPs complexes; red fluorescence is from *Syne* (λ_{ex} = 488 nm, λ_{em} = 650−750 nm), blue fluorescence is from PFBT-NPs (λ_{ex} = 488 nm, λ_{em} = 500−600 nm).

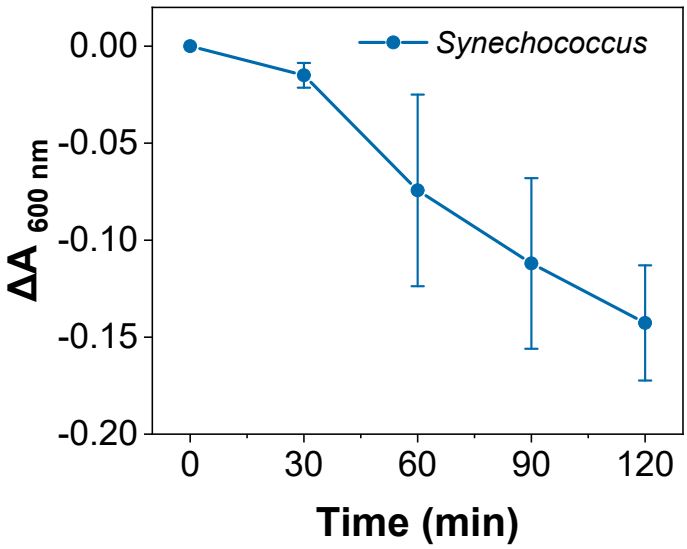

Figure S6. The absorption changes of DCPIP at 600 nm for *Syne* irradiated by ECL.

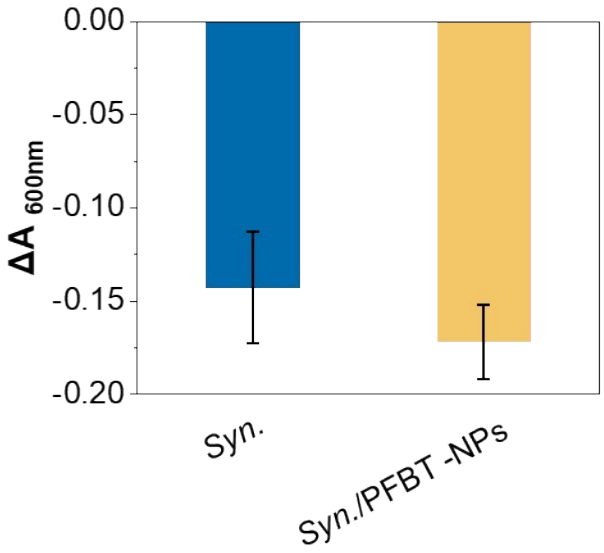

Figure S7. The DCPIP reduction rates of *Syne* and *Syne*/PFBT-NPs, respectively.

Table S1. Chlorophyll fluorescence parameters of *Syne* and *Syne*/PFBT-NPs complexes under dark adaptation.

Parameter	Definition	*Syn.*	*Syn.*/PFBT-NPs
F_v/F_m	maximal quantum yield of PSII under dark adaptation	0.131	0.142
PI abs	energy conversion from photons of PSII to reducing electron acceptors	0.004	0.004
PI total	energy conversion from photons of PSII to reducing electron acceptors	0.0031	0.0036
ABS/RC	energy conversion from photons of PSII to reducing PSI and electron acceptors	18.0837	18.4047
TR_o/RC	absorbed energy per reaction center	2.5086	2.5455
ET_o/RC	trapped energy per reaction center	0.7263	0.7917
RE_o/RC	energy used for electron transfer per reaction center	0.372	0.399
ABS/CS_m	energy transported to PSI per reaction center	1069	1116
TR_o/CS_m	absorbed energy per cross section	140	153
ET_o/CS_m	trapped energy per cross section	39	43
RE_o/CS_m	energy used for electron transfer per cross section energy transported to PSI per cross section	22	24
$\Delta(R_o)$	the efficiency of electron transfer to PSI	0.5263	0.5581