Supporting Information

A Rhythmic Assembly System with Fireflies’ Function Based on Reversible Formation of Dynamic Covalent Bonds Driven by A pH Oscillator **

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Part I  Experimental details

1 Materials

Phenylboronic acid (PBA), Alizarin Red S (ARS) and hydrogen peroxide ($H_2O_2$) (30 wt. %) were purchased from J&K chemicals (Beijing, China). Sodium dithionite ($Na_2S_2O_4$) was purchased from Aladdin Co., Ltd (Shanghai, China). The water used in this study was distilled and further purified using a filtration system.

2 Construction of an HPD pH oscillator

2.1 Reactor

The pH-oscillating system used in our studies was based on the sulfur oscillatory mechanism under a continuously stirred tank reactor (CSTR). [1] The CSTR is a cylindrical-shaped glass reactor with a liquid volume of 20 mL with two input tubes and two output tubes, as shown in Figure S1 (b). The reactor was closed with a silicon cap. A combination pH meter and a thermometer connected to a computer were led through the cap. The batch experiments were performed in a cylindrical-shaped thermostatic glass vessel with a liquid volume of 50 mL.

![Figure S1](image)

Figure S1 The experimental setup (a) and the CSTR of the HPD pH oscillation reaction

2.2 Procedures

Sodium dithionite (7.5 mmol/L) ($Na_2S_2O_4$) with pH 12 and hydrogen peroxide (23 mmol/L) ($H_2O_2$) solutions were prepared separately using deionized water in 250 mL volumetric flasks. Throughout the experiments, the solution of sodium dithionite in its reservoir was bubbled with nitrogen gas to prevent autoxidation. The
The experimental setup for the pH oscillator was shown in Figure S1 (a). The oscillating reactions were carried out at 22 °C in the CSTR. Reactant solutions were pumped into the reactor through the inlet tubes by means of a peristaltic pump (DESAGA). The excess reaction mixture was removed with the same pump through two outlet tubes. A magnetic stirrer at a constant stirring rate was used to ensure uniform mixing. The maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered to the desired value. The reactions in the batch system were initiated by the addition of the H$_2$O$_2$ solution. The pH-time data was monitored by a pH meter connected to a computer using a REXDC 1.0 data collection software package. [2]

3 References


Part II  Other supporting materials

Video S1 This video shows reversible, autonomic and sustainable assembly/disassembly behavior accompanying cyclic fluorescence/non-fluorescence oscillation, which works in a similar fashion as observed in the body of the fireflies. Playback speed is 20×