Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

The fabrication of supra-amphiphile for dissipative self-assembly

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1. The complex formed by PEG and iodine

The binding of PEG homopolymer and iodine can turn PEG from hydrophilic to hydrophobic, leading the precipitation of their complex. Figure S1 shows the brown precipitation of their complex.

Figure S1. The precipitation of the complex formed by PEG ($M_w = 6000$) and iodine.

2. The original intensity-time curve of the scattering light.

As the oscillations also generated N_2O and N_2, the rising bobbles in the CSTR would sometimes cause a random and momentary increase of the scattering light as shown in Figure S2b. For the convenience of disscusion, in the Figure 4b, the abnormal data points of the curve were removed.

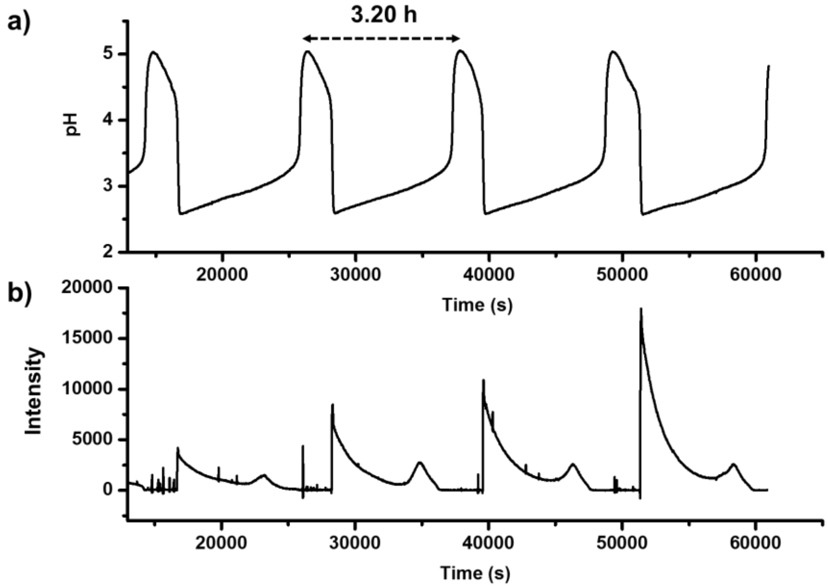

Figure S2. a) The pH-time curve of the oscillations. b) The original intensity-time curve of the scattering light.

3. The investigation of the the increase in scattering intensity with repeated oscillation cycles

According to the Rayleigh's equation, the intensity of the scattering light, $I \propto d^6$, where d is the diamater of the aggregates. It means that the intensity of the scattering light will increase significantly if larger aggregates appear in the solution, even though the amount of the larger aggregates is small. Unfortunately, Both TEM and DLS is difficult to detect the diameter of the aggregates in CSTR directly, becaues the reaction mixture in CSTR will fall into thermodynamic equilibrium very fast once it is drawn out. Nevertheless, we still tried to perform the following experiment to investigate the increase of the diameter and scattering light.

The PEG(I_2)-*b*-PLKC solution was prepared by adding 8.0 μM PEG-*b*-PLKC in the solution of iodine (the concentration of iodine was 1 mM and pH was 2.9). If both NaOH and NH_2OH HCl were added into the solution of PEG(I_2)-*b*-PLKC, the solution got transparent because the iodine was reduced to I^-. The pH of the transparent solution was measured as about 6. As shown in Figure S3, if proper amounts of $NaIO_3$ and HCl were added to the transparent solution to recover the low pH and iodine, the DLS measurement showed that the average diameter of the reappeared aggregtes got larger (from 35 nm to 70 nm), leading to the increase of the scattering light.

Although the chemical ocsillations in CSTR is a metabolic and non-quilibirum system, the above experiment still suggests that larger aggregates will generate, accumulate and even grow with every ocsillation cycles leading increase of the scattering light.

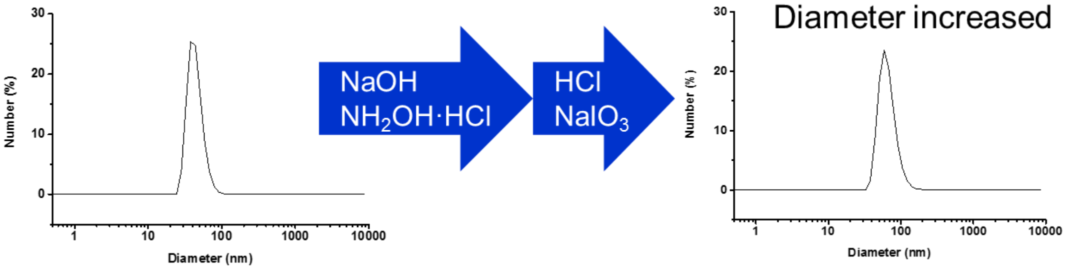

Figure S3. “Irreversibility” of the self-assembly and disassembly of PEG(I_2)-*b*-PLKC.

4. The simulation of the IO_3^--NH_3OH^+-OH oscillation without PEG-*b*-PLKC

The simulations were carried out with a commercial software package (Berkeley Madonna, Rosenbrock(still) with error control parameter set at 10^{-10}) for stiff differential equations.

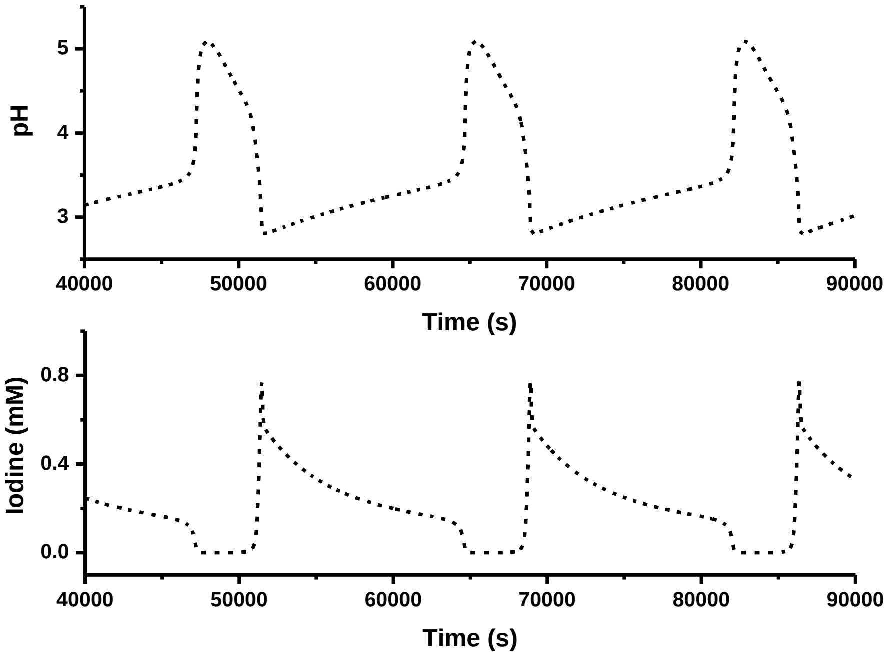

Figure S4. Simulation of the IO_3^--NH_3OH^+-OH^- oscillation, input concertration: $[NH_2OH \cdot HCl]_0$ = 50 mM, $[NaIO_3]_0$ = 13mM, $[NaOH]_0$ = 40 mM, $k_0 = 1.78\times10^{-4}$ s^{-1}. The period was simulated as 4.8 h.

5. The measurement of the equilibrium constant of reaction 9, K_{M9} by isothermal titration calorimetry (ITC)

ITC measurement was performed to obtain the equilibrium constant of reaction 9 in Table 1, K_{M9}, which is actually the equilibrium constant of the non-covalent interaction between iodine and PEG-*b*-PLKC. The concentration of iodine was 10 mM, and the concentration of PEG-*b*-PLKC was 0.2 mM (calculated by the repeating units). The pH of the two solution were both 2.9. The titration curve is shown in Figure S5, pK is determined as 3.5.

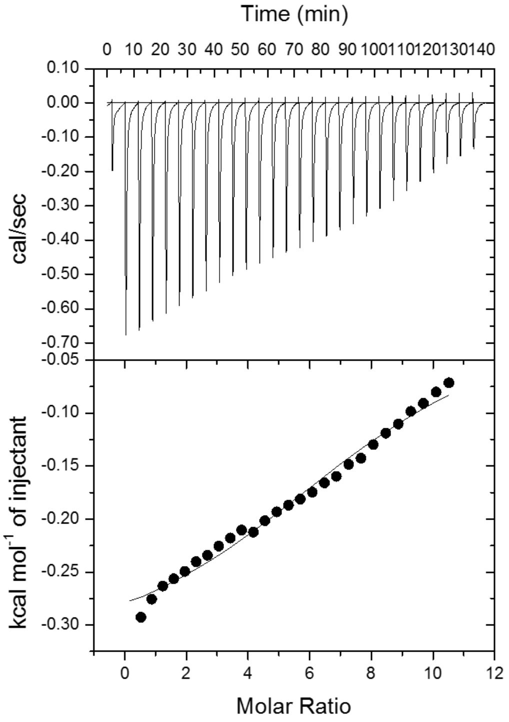

Figure S5. The measurement of the equilibrium constant of the non-covalent interaction between iodine and PEG-*b*-PLKC by ITC, T = 298 K.

6. Scattering without PEG-*b*-PLKC in CSTR

Scattering light was quite weak without PEG-*b*-PLKC, during the low-pH state of the oscillation, indicating that no aggregates formed.

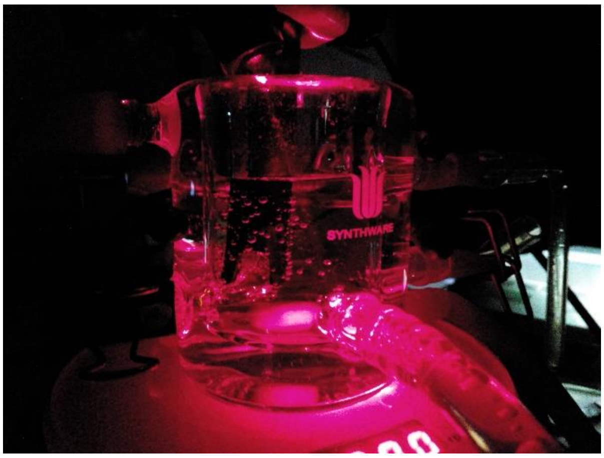

Figure S6. Scattering light during the low-pH state of the oscillation without PEG-*b*-PLKC