Electronic Supplementary Information (ESI) available for:

Photophobic and phototropic movement of a self-oscillating gel

Xingjie Lu,[a] Lin Ren,[a] Qingyu Gao,[a] Yuemin Zhao,[a] Shaorong Wang,[a] Jiaping Yang[a] and Irving R. Epstein*[b]*

a College of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, (China)

b Department of Chemistry and Volen Center for Complex Systems, MS 015, Brandeis University, Waltham, Massachusetts 02454-9110, (USA)

Supporting Information

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1. Experimental details for synthesizing the BZ gel

1.1 Materials.

N-Isopropyl acrylamide (NIPAAm, Tokyo Chemical Industry Co., Inc.), N,N'-methylenebisacrylamide (MBA, Sigma-Aldrich), 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Sigma-Aldrich), 2,2'-azobis (isobutyronitrile) (AIBN, Sigma-Aldrich), ruthenium (4-vinyl-4'-methyl-2,2`-bipylridine) bis(2,2`-bipyridine) bis (hexafluorophosphate) ($Ru(bpy)_3$, were synthesized according to established protocols[1-3]). Other reagents were purchased from Sinopharm Chemical Co. Ltd.

1.2 Fabrication of BZ gel in capillary.

The BZ gel was synthesized in a capillary of inner diameter of 1.0 ± 0.1 mm according to previous work [4]. NIPAAm (0.305 g), $Ru(bpy)_3$ (37.8 mg), AIBN (4.6 mg) and MBA (2.2 mg) were dissolved in 1.0 mL of methanol, and AMPS (10.2 mg) was dissolved in 1.0 mL of distilled water (both solvents were previously purged with N_2). The solutions were mixed and injected into the capillary. The open end of the capillary was sealed with PVC and then polymerized at 60.0 °C for 24 h. After gelation, the capillary was cut into small sections (5.0-6.0 mm in length). The resulting BZ gel was soaked in pure methanol for a week to remove unreacted monomers and then hydrated by immersing in a graded series of methanol/water mixtures for 1 day each in 100%, 75%, 50%, 25% and 0% methanol in water. Finally, we obtained the pure one dimensional poly(NIPAAm-co-$Ru(bpy)_3$-co-AMPS) gel.

2. Experimental OPR curves

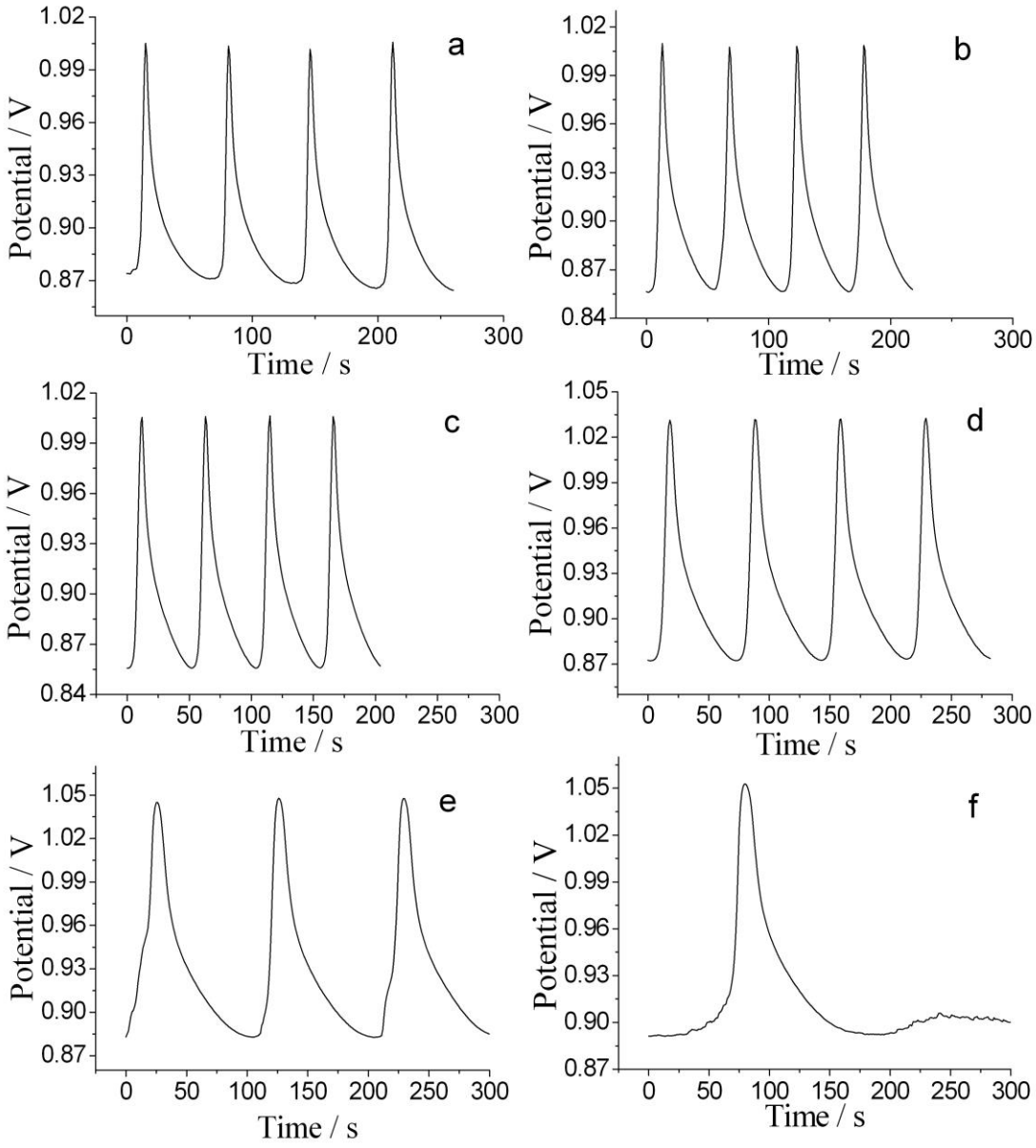

Fig. S1 Dependence of oscillatory frequency of bulk system on light intensity. a: I = 1.65 μW cm^{-2}, frequency = 0.01524 s^{-1}; b: I = 52 μW cm^{-2}, frequency = 0.01813 s^{-1}; c: I = 280 μW cm^{-2}, frequency = 0.01951 s^{-1}; d: I = 2810 μW cm^{-2}, frequency = 0.01413 s^{-1}; e: I = 4410 μW cm^{-2}, frequency = 0.00984 s^{-1}; f: I = 5200 μW cm^{-2}, frequency = 0 s^{-1}. Other experimental conditions are the same as Fig. 1.

3. Model and Simulation

Amemiya *et al.*[5] introduced a three-variable photosensitive Oregonator model to describe both photoinduction and photoinhibition in the ruthenium-catalysed BZ reaction. The equations were nondimensionalized by using the Tyson scaling[6].

$$\begin{cases} \varepsilon \dfrac{\mathrm{d}x}{d\tau} = x(1-x) + y(q-x) - \varepsilon k_f x + \phi P_2 \\ \varepsilon' \dfrac{dy}{d\tau} = -y(q+x) + fz + \varepsilon' k_f (y_0 - y) + \phi P_1 \\ \dfrac{dz}{d\tau} = x - z - k_f z + \phi\left(\dfrac{P_1}{2} + P_2\right) \end{cases} \quad \text{(I)}$$

In the equations, y_0 is the nondimensionalized concentration of Br^- in the feed flow solution; k_f is the flow rate, ϕ is the light flux, P_1 and P_2 are the factors for photoinhibition and photoinduction, respectively. By applicating a steady state approximation for *y*, the above equations can be reduced to a two-variable Oregonator model (II). Because our experiments were carried out in a batch system, we set $k_f = 0$. The resulting equations have the following form:

$$\begin{cases} \varepsilon \dfrac{dx}{d\tau} = x(1-x) + (fz + \phi P_1)(q-x)/(q+x) + \phi P_2 \\ \dfrac{dz}{d\tau} = x - z + \phi\left(\dfrac{P_1}{2} + P_2\right) \end{cases} \quad \text{(II)}$$

In our numerical simulations, we set $f = 1.02$, $\varepsilon = 0.03314$ and $q = 1.0 \times 10^{-4}$. Values for P_1 and P_2 were taken from the literature[5], i.e., $P_1 = 0.0124$, $P_2 = 0.77$. The ODEs were numerically integrated with an explicit fourth-order Runge-Kutta method with time step 1.0×10^{-5}. Adjusting the parameter ϕ results in changes in the oscillation frequency similar to those seen in the experiments with changing illumination intensity.

References

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