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Oscillating Luminescence in a $Ru(bpy)_3^{2+}$ Langmuir Monolayer on the Belousov–Zhabotinskii Reactor

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We report herein the observation of oscillating fluorescence images in a $Ru(bpy)_3^{2+}$ Langmuir monolayer spread on the surface of the Belousov–Zhabotinskii (BZ) reactor. The $Ru(bpy)_3^{2+}$-catalyzed BZ reaction has received much recent interest in the field of nonlinear chemical oscillation. $Ru(bpy)_3^{2+}$ not only serves as a luminescent redox indicator[1,2] but, due to its peculiar photochemical properties, makes the reaction system extremely sensitive to photoirradiation.[3,4] The light-sensitive nature has been successfully utilized to produce a new kind of photochemical memory device,[5] an image processor,[6] and new spatial patterns of traveling waves.[7,8] In these studies, homogeneously-mixed bulk solutions have been predominantly employed at least as a starting medium. This situation has motivated us to see how the character of temporal and spatial oscillations will be modified on introducing spatial distributions or anisotropies to the BZ reaction system. Such heterogeneities can be most readily established by coupling the BZ reactor with Langmuir monolayers of catalytic or other reactant chemicals.

A surfactant derivative of $Ru(bpy)_3^{2+}$, $(bpy)_2Ru^{II}[bpy(COOC_{18}H_{37})_2]^{2+}(PF_6^-)_2$ (where the carboxy substituents are in the 4,4′ position), was synthesized by a literature method.[9] Monolayers of this compound were spread from chloroform solution onto an unstirred reactor surface in a Teflon-coated trough (25 × 10 cm) placed on the stage of a fluorescence microscope (Olympus BHMS). The monolayer was illuminated with blue exciting light (410–490 nm), and the resultant fluorescence emission was detected using the microscope with the help of a SIT television camera.[10] This method allowed direct visualization of the two-dimensional distribution of fluorescence intensity in the monolayer.

The reactant solution for the monolayer substrate was prepared by adding H_2SO_4, $NaBrO_3$, $CH_2(COOH)_2$, $Ce(NH_4)_2(NO_3)_6$, and $HClO_4$ in this order to pure water in a beaker. The solution was stirred until Ce^{4+}–Ce^{3+} oscillations started after an initial induction period, and then the solution was poured immediately into the trough to give a layer of 6-mm depth for monolayer studies. ClO_4^{-1} was added in order to enhance the luminescence intensity of the $Ru(bpy)_3^{2+}$ monolayer.[11,12] We were unable to observe clear fluorescence images in the absence of ClO_4^{-1}. The bulk reaction was monitored by recording the potential from a platinum electrode simultaneously with the fluorescence observation. All experiments were carried out at a temperature of 26 ± 1 °C.

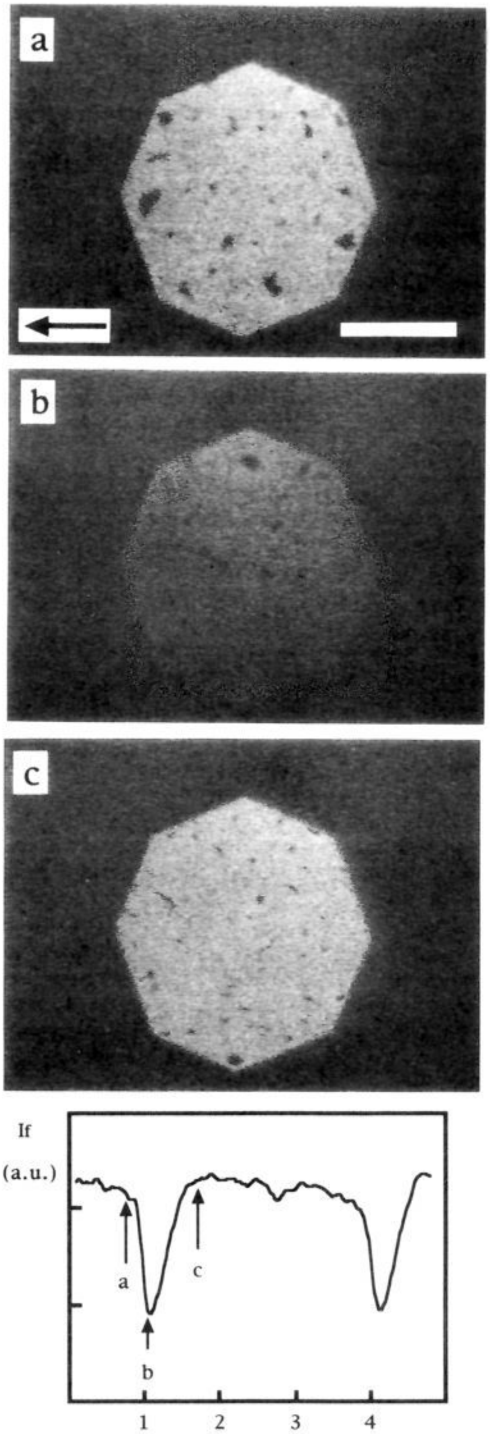

Figure 1. Luminescence oscillations of a $Ru(bpy)_3^{2+}$ monolayer on the BZ reactor. Fluorescence microscope images (a–c) were taken at a surface pressure of 1 mN/m. Initial composition of the reactor: $[H_2SO_4] = 0.36$ M, $[NaBrO_3] = 0.04$ M, $[CH_2(COOH)_2] = 0.1$ M, $[Ce(NH_4)_2(NO_3)_6] = 0.001$ M, and $[HClO_4] = 0.1$ M. The arrow indicates the scanning direction for microscope observation. The bar in panel a marks 100 μm. In the bottom panel is shown the corresponding trace of the fluorescence intensity (I_f) obtained by measuring the luminescence from the monitor screen with a multichannel spectrophotometer.

Figure 1 shows typical fluorescence images of the $Ru(bpy)_3^{2+}$ monolayer taken at suitable time intervals. The octagonal area represents a microscope field illuminated by strong exciting light. During the microscope observation, the exciting light was scanned

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Table I. The Period of Fluorescence and Potential Oscillations for Various $NaBrO_3$ Concentrations[a]

	period/s	
$[NaBrO_3]$/M	fluorescence	potential
0.16	72 ± 3	49 ± 2
0.08	103 ± 6	74 ± 2
0.04	168 ± 9	110 ± 8

[a] Concentrations of other chemicals are the same as in Figure 1. Each period is averaged over five cycles.

across the monolayer at a speed of 15 μm/s in order to minimize photodegradation of the $Ru(bpy)_3{}^{2+}$ molecules. In Figure 1a, the white and black phases correspond to luminescent $Ru(bpy)_3{}^{2+}$ crystallites and vacant domains formed between the boundaries of these crystallites, respectively. The white area turns suddenly dark in Figure 1b, indicating that $Ru(bpy)_3{}^{2+}$ is now effectively oxidized to nonluminescent $Ru(bpy)_3{}^{3+}$. As time progresses, $Ru(bpy)_3{}^{2+}$ regenerates and the dark image gradually becomes fluorescent again (Figure 1c). These bright–dark image transitions are found to recur periodically.

The major driving force for the $Ru(bpy)_3{}^{2+}$–$Ru(bpy)_3{}^{3+}$ oscillations is thought to be the Ce^{4+}–Ce^{3+} oscillations in the subphase. However, systematic studies reveal that the oscillating fluorescence in the $Ru(bpy)_3{}^{2+}$ monolayer has larger periods compared to the oscillating potential in the bulk solution (Table I). This discrepancy suggests a lengthening of the oscillation period in the BZ reactor just under the $Ru(bpy)_3{}^{2+}$ monolayer. The lengthening may be interpreted in part as arising from such interfacial effects as efficient O_2 absorption and/or Br_2 loss at the gas–liquid interface,[13,14] or modification of the reactant concentrations near the reactor surface due to the existence of a densely-charged $Ru(bpy)_3{}^{2+}$ monolayer. Of course we cannot rule out the possibility that $Ru(bpy)_3{}^{2+}$ is involved directly in the BZ reaction as a catalyst and changes its oscillatory behavior at the reactor surface.

Unless the monolayer is too intensely illuminated, the fluorescence oscillation occurs almost simultaneously in the whole microscope field in the early stages of the reaction. Due to the absence of stirring, however, spatial inhomogeneities are produced in the reactant solution after several cycles of oscillation. Consequently, we sometimes observe the reaction to proceed as a dark oxidized band passing through the illuminated field as a phase wave. At more intense illumination, which can be achieved experimentally by widening the microscope field or by decreasing the scanning speed, in-phase fluorescence oscillations become hardly observable. The oscillation period tends to be greater in the illuminated area than in a nonilluminated or less-illuminated area. Therefore, the darkening of the fluorescence image is seen to propagate in the direction opposite to the scanning direction, starting at the field boundary through which the $Ru(bpy)_3{}^{2+}$ monolayer is freshly coming into the illuminated region, and then spreading to the rest of the field. In this case, the darkening is even entirely suppressed in a portion of the monolayer subject to sufficient illumination (Figure 2). Such inhomogeneities are presumably induced by the inhibitory effect of illumination resulting from excess Br^- production in the photochemical reaction of $Ru(bpy)_3{}^{2+}$.[4,6]

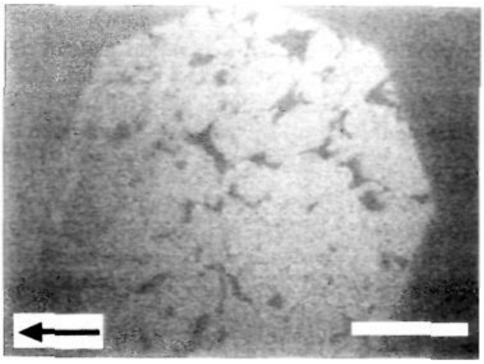

Figure 2. Fluorescence microscope images of a $Ru(bpy)_3{}^{2+}$ monolayer. Experimental conditions and notations are as in Figure 1. The darkening takes place periodically at the field boundary (left side), but the rest of the field remains relatively fluorescent throughout the observation.

The present findings demonstrate that the $Ru(bpy)_3{}^{2+}$ monolayer can indeed interact with the BZ-type subphase via oscillatory oxidation–reduction reactions. Such an interplay has also been found to be photochemically controllable by the action of an external light signal. The technique of fluorescence microscopy is extremely useful in studying the BZ reactor–monolayer coupled system because it provides direct information on the spatiotemporal structures at the air–water interface at the micrometer level. A more thorough investigation is underway using this technique in the context of spatial pattern formation, which might reveal further new details of the oscillatory behavior in the coupled system.

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