

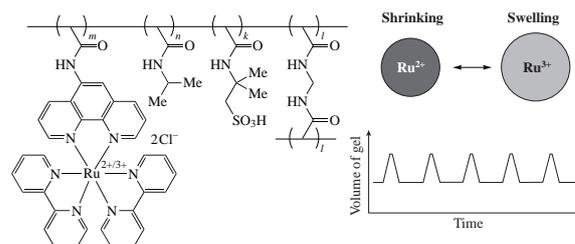
## Self-oscillating gels based on novel catalyst for the Belousov–Zhabotinsky reaction

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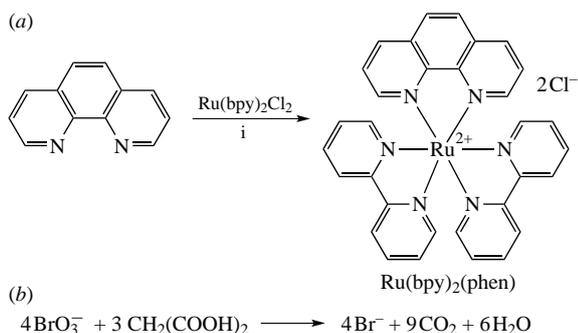
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We report on the synthesis of new  $\text{Ru}(\text{bpy})_2(\text{phen})$  catalyst for the oscillatory Belousov–Zhabotinsky chemical reaction and on the preparation of novel  $\text{Ru}(\text{bpy})_2(\text{phen})$ -based self-oscillating gels. The synthesized gels exhibit high-amplitude autonomous mechanical oscillations when the Belousov–Zhabotinsky reaction proceeds inside these gels.



**Keywords:** nonlinear chemistry, Belousov–Zhabotinsky reaction, ruthenium complexes, polymers, self-oscillating gels.

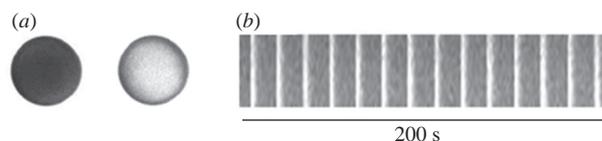
Development of self-oscillating polymer gels driven by the oscillatory Belousov–Zhabotinsky (BZ) reaction is an actively developing research direction.<sup>1,2</sup> Such self-oscillating gels have potential application in the design of soft robots and artificial muscles (actuators).<sup>3–6</sup> To synthesize self-oscillating gels, most researchers use ruthenium(II) tris(2,2'-bipyridyl) complex,  $\text{Ru}(\text{bpy})_3$ , as the catalyst for the BZ reaction, when  $\text{Ru}(\text{bpy})_3$  part is covalently bound to or is incorporated into the polymeric network of the gel.<sup>7,8</sup> When such a gel is immersed in an aqueous catalyst-free BZ solution (CFBZ), the oscillatory BZ reaction starts inside the gel generating autonomous periodic redox transitions of the  $\text{Ru}(\text{bpy})_3$ . These transitions induce in their turn the periodic changes in the volume of the gel, *i.e.*, mechanical oscillations. In addition to  $\text{Ru}(\text{bpy})_3$ , complexes of  $\text{Ru}^{\text{II}}$  with terpyridine ligands are also used to create self-oscillating gels,<sup>9</sup> although gels based on them demonstrate low-amplitude mechanical oscillations. There are other interesting heteroligand  $\text{Ru}^{\text{II}}$  complexes, for example, ruthenium(II)-2,2'-bipyridine-1,10-phenanthroline-3,8-dicarboxylic acid.<sup>10</sup> However, until now, heteroligand complexes based on bis(2,2'-bipyridine)(1,10-phenanthroline)ruthenium(II) have not been used as catalysts for the BZ reaction and even more so, self-oscillating gels based on them were not created.



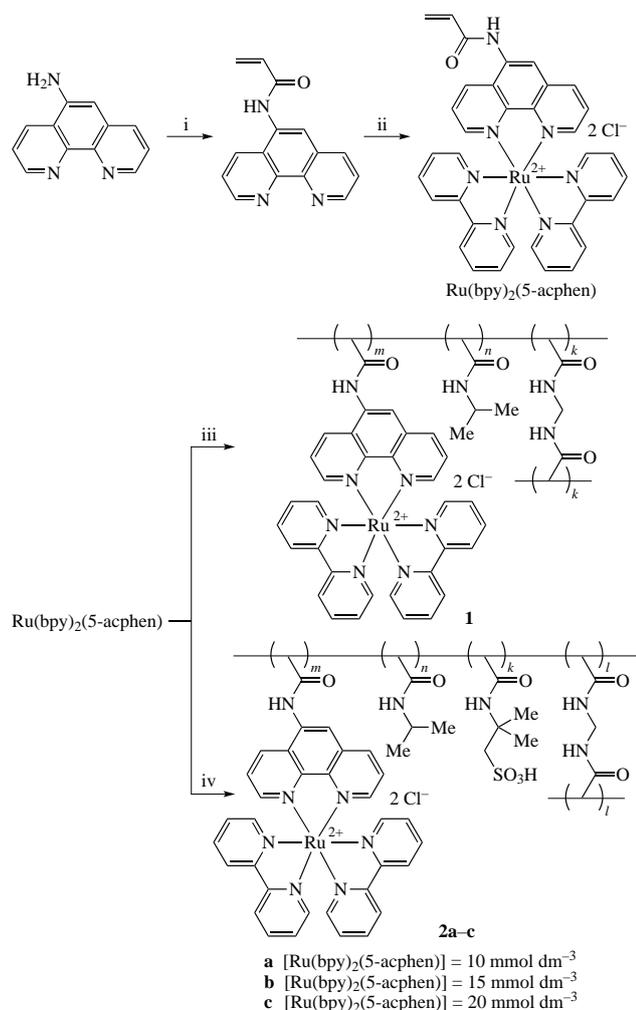
**Scheme 1** (a) Synthesis of  $\text{Ru}(\text{bpy})_2(\text{phen})$ . Reagents and conditions: i, EtOH, 70 °C, 11 h. (b) Gross scheme of the BZ reaction catalysed in our case by  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex.

Herein, we report on the synthesis of bis(2,2'-bipyridine)-(1,10-phenanthroline)ruthenium(II) complex,  $\text{Ru}(\text{bpy})_2(\text{phen})$ , its testing as a new catalyst for the BZ reaction, and on the creation of new self-oscillating gels obtained by copolymerization of acrylamide derivative of the  $\text{Ru}(\text{bpy})_2(\text{phen})$  with 2-acrylamido-2-methylpropanesulfonic acid (AMPS), *N*-isopropylacrylamide (NIPA), and *N,N*-methylenebisacrylamide (MBA). First, the  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex [Scheme 1(a)] was synthesized. To test  $\text{Ru}(\text{bpy})_2(\text{phen})$  as a catalyst for the BZ reaction [see Scheme 1(b)], the aqueous solution of all the BZ-reagents, including the  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex, is dispersed in fluorinated oil with the addition of surfactant (the initial concentrations of the reagents in the BZ solution are given in captions to Figure 1). As a result, droplets of the BZ mixture were obtained [see Figure 1(a)]. These droplets demonstrate an oscillatory dynamics typical of the BZ reaction [see Figure 1(b)]. This experiment shows that the  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex can serve as the catalyst for the BZ reaction (for all experimental details, see Online Supplementary Materials).

To incorporate the  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex into the polymer chain, we synthesized its derivative, bis(2,2'-bipyridine)(5-acrylamido-1,10-phenanthroline)ruthenium(II),  $\text{Ru}(\text{bpy})_2(5\text{-acphen})$  (Scheme 2). The acrylamide fragment introduced into the structure of the  $\text{Ru}(\text{bpy})_2(\text{phen})$  complex provides the copolymerization of the resulting  $\text{Ru}(\text{bpy})_2(5\text{-acphen})$  compound



**Figure 1** (a) Snapshots of an isolated BZ droplet (diameter 150  $\mu\text{m}$ ) containing  $\text{Ru}(\text{bpy})_2(\text{phen})$  in the reduced (dark) and oxidized (light) states. (b) Space-time plot for oscillations of this BZ droplet (oscillation period is 15 s). Vertical white bars in space-time plot present oxidized states of the  $\text{Ru}(\text{bpy})_2(\text{phen})$ , dark bars present the reduced states. Concentrations of the reagents in the CFBZ solution:  $[\text{MA}] = 0.36\text{ M}$ ,  $[\text{NaBrO}_3] = 0.27\text{ M}$ ,  $[\text{NaBr}] = 0.07\text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 1.2\text{ M}$ ,  $[\text{Ru}(\text{bpy})_2(\text{phen})] = 3\text{ mM}$ . The space-time plot is built along the line passing through the centre of the droplet.

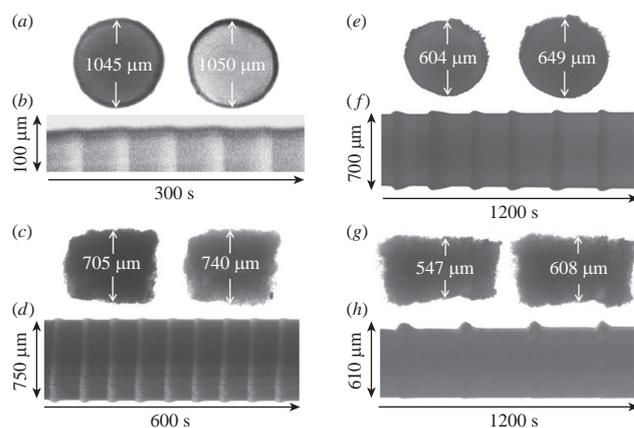


**Scheme 2** Reagents and conditions: i, CH<sub>2</sub>=CHC(O)Cl, TMEDA, THF, 10 °C, 20 h; ii, Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, EtOH, 70 °C, 11 h; iii, *N*-isopropylacrylamide (NIPa), *N,N'*-methylenebisacrylamide (MBA), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, TMEDA; iv, NIPa, MBA, CH<sub>2</sub>=CHC(O)NHC(Me)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H (AMPS), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, DMSO, H<sub>2</sub>O, 65 °C, 1 h.

with other acrylamide derivatives, for example, NIPa and/or MBA. Copolymerization of Ru(bpy)<sub>2</sub>(5-acphen) complex with NIPa and MBA afforded gel **1** in which Ru(bpy)<sub>2</sub>(5-acphen) serves as a catalytic fragment, NIPa as a monomer forming a polymer chain, and MBA as a cross-linker.

To test the properties of gel **1**, the latter was synthesized in the form of a transparent homogeneous microsphere [Figure 2(a)], which was immersed in the aqueous CFBZ solution. The concentrations of BZ reagents in the CFBZ solution were the same as those used previously<sup>6</sup> for testing gels based on the Ru(bpy)<sub>3</sub> complex. In the aqueous CFBZ solution, gel **1** exhibits oscillatory behavior [see Figure 2(b)]. The microsphere diameter increases when Ru(bpy)<sub>2</sub>(phen) fragment exists in the oxidized state and decreases when it is in the reduced state. The amplitude of mechanical oscillations is small, about 0.5%, if the diameter of the microspheres is recorded, and about 1.5% if we measure volume changes.

To increase the amplitude of mechanical oscillations, we used the fact that gels with a microphase-separated structure exhibit more significant mechanical oscillations than gels with a homogeneous structure.<sup>11,12</sup> To synthesize such a microphase-separated gel, we copolymerized Ru(bpy)<sub>2</sub>(5-acphen) simultaneously with three different monomers: AMPS, NIPa, and MBA. Chemical structure of the synthesized microphase-separated gel **2a** is presented in Scheme 2. Gel **2a** contains about 10 mmol dm<sup>-3</sup> of Ru(bpy)<sub>2</sub>(5-acphen). A piece of gel **2a** which



**Figure 2** Oscillations of pieces of gels in the CFBZ solution with the following concentrations: [MA] = 0.063 M, [NaBrO<sub>3</sub>] = 0.084 M, [HNO<sub>3</sub>] = 0.9 M. (a), (c), (e), (g) Snapshots of pieces of gels **1**, **2a**, **2b**, and **2c**, respectively, in the shrunken state (left snapshot) (reduced state of the catalyst) and in the swollen state (right snapshot) (oxidized state of the catalyst). (b) Space-time plot of the top edge of the microsphere of gel **1** taken along the diameter. (d), (f), (h) Space-time plots of the oscillations of gels **2a**, **2b**, and **2c**, respectively. Space-time plots are obtained at 450 nm, where Ru(bpy)<sub>2</sub>(5-acphen) has the maximum absorption and taken along the lines indicated by the white arrows. Period of the oscillations  $T/s \equiv$  (b) 55, (d) 67, (f) 195, (h) 300. Vertical white (dark) bars in the space-time plot present the oxidized (reduced) state of the catalyst.

is opaque [see Figure 2(c)] exhibits pronounced self-oscillatory behavior in the CFBZ solution [see Figure 2(d)] becoming lighter (darker) in the oxidized (reduced) state of the catalyst. Accordingly, gel **2a** expands (shrinks) when the catalyst exists in the oxidized (reduced) state; the mechanical oscillations of the gel coincide with the chemical ones. The changes of the linear (volume) size of the piece of gel **2a** is about 5 (15)%.

To further increase the amplitude of mechanical oscillations, we have synthesized gels **2b** and **2c** having the same chemical structure as gel **2a** (see Scheme 2), but containing about 15 and 20 mmol dm<sup>-3</sup> of Ru(bpy)<sub>2</sub>(5-acphen), respectively. Since gels **2b,c** are almost opaque, it is difficult to observe chemical oscillations in the CFBZ solution by the optical method, but mechanical oscillations are clearly visible [see Figure 2(e)–(h)]. The periodic changes of the linear (volume) size of the piece of gel **2b** is about 7 (21%). Oscillatory behavior of self-oscillating gel **2b** is demonstrated in movie ‘Ball of gel **2b**’ (see Online Supplementary Materials, Figure S7, Video sped up 48 times). For mechanical oscillations of gel **2c**, linear and volume changes are even greater, about 10 and 30%, respectively. The period of oscillations also increases with an increase in the content of Ru(bpy)<sub>2</sub>(5-acphen) in the gel (see captions to Figure 2).

In conclusion, we have demonstrated that Ru(bpy)<sub>2</sub>(phen) heteroligand complex can be used as a catalyst for the BZ reaction. With this complex, it is possible to prepare self-oscillating gels demonstrating chemical-mechanical oscillations under the conditions of the BZ reaction. The changes of the linear (volume) size of the pieces of self-oscillating gel are about 5–10% (15–30%). Gels with such a large amplitude of mechanical oscillations can be used in the development of chemomechanical devices such as self-actuating gel pumps<sup>13</sup> or hydrogel-based motors.<sup>14</sup>

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### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.025.

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