

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

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### **1. Catalyst synthesis. Part I**

For the synthesis, we used the following chemicals (all from Aldrich, analytical grade) without further purification: bis(2,2'-bipyridine)ruthenium(II)dichloride, acryloyl chloride, 1,10-phenanthroline-5-amine, phenanthroline, tetrahydrofuran, benzene, ethyl acetate, ethanol, methylene chloride, tetramethylethylenediamine, as well as distilled water. Column chromatography is performed using Merck silica gel 60 as a sorbent.  $^1\text{H}$  NMR spectra of the obtained substances are recorded on a Bruker Avance III 400 MHz at temperature 23 °C in the Fourier transform mode with the chemical shifts being reported in ppm downfield from tetramethylsilane (TMS).

The following abbreviations to describe  $^1\text{H}$  NMR spectra are used:  $\delta$  = chemical shift expressed in parts per million (ppm) by frequency,  $J$  = spin-spin coupling constant stated in Hz, s = singlet, d = doublet, t = triplet, m = multiplet or multiple signals, dd = double doublet. As a solvent for the NMR measurement, we used  $(\text{CD}_3)_2\text{SO}$  (= DMSO- $d_5$ ). UV-visible absorption spectra are measured on a UV-3100 spectrophotometer. Elemental analysis is done using microanalysis methods.

*Synthesis of 5-acrylamido-1,10-phenanthroline.* In this synthesis, 1,10-phenanthroline-5-amine (58.6 mg, 0.300 mmol) is added to a solution of tetramethylethylenediamine (29.9  $\mu\text{l}$ , 23.2 mg, 0.200 mmol) in dry THF (9 ml). The suspension is stirred at 10 °C for 1 h. Then a solution of acryloyl chloride (28.5  $\mu\text{l}$ , 31.9 mg, 0.352 mmol) in THF (1 ml) is slowly added at 10 °C. The mixture obtained is kept stirring at 10 °C for 20 h. The solvent is evaporated. Purification by column chromatography on silica gel (EtOH/ $\text{CH}_2\text{Cl}_2$ , 1:7) gives 5-acrylamido-1,10-phenanthroline (37.0 mg, 0.148 mmol) as the yellow powder, yield ~49%.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  10.33 (s, 1H, NH), 9.13 (d,  $J$  = 2.8 Hz, 1H, phen-H), 9.03 (d,  $J$  = 4 Hz, 1H, phen-H), 8.60 (dd,  $J$  = 8 Hz,  $J$  = 0.8 Hz, 1H, phen-H), 8.45 (dd,  $J$  = 8 Hz,  $J$  = 1.2 Hz, 1H, phen-H), 8.29 (s, 1H, phen-H), 7.87-7.78 (m, 1H, phen-H), 7.77-7.68 (m, 1H, phen-H), 6.79-6.64 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 6.35 (d,  $J$  = 16.8 Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 5.86 (d,  $J$  = 10.4 Hz, 1H,  $\text{CH}=\text{CH}_2$ ), see Figure S1. The  $^1\text{H}$  NMR data are similar to those reported.<sup>S1</sup> Elemental analysis data for  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}$  (%): calculated C 72.28, H 4.45, N 16.86; found C 72.31, H 4.50, N 16.83.

*Synthesis of bis(2,2'-bipyridine)(1,10-phenanthroline)ruthenium(II) dichloride Ru(bpy)<sub>2</sub>(phen).* Bis(2,2'-bipyridine)ruthenium(II) dichloride (200.0 mg, 0.413 mmol) and phenanthroline (89.0 mg, 0.494 mmol) are mixed in EtOH (10 ml). The mixture is kept stirring at 70 °C for 11 h. The mixture is then cooled and filtered, the filtrate obtained is evaporated in vacuum. The residue is dissolved in H<sub>2</sub>O (5 ml), and unreacted phenanthroline is extracted with benzene (4×10 ml). The water solution is evaporated to leave Ru(bpy)<sub>2</sub>(phen) (240.6 mg, 0.362 mmol) as a red powder, yield 88%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 8.88 (d, J = 8.0 Hz, 2H, phen-H), 8.83 (d, J = 8.0 Hz, 2H, bpy-H), 8.79 (d, J = 8.2 Hz, 2H, bpy-H), 8.37 (s, 2H, phen-H), 8.20 (t, J = 7.6 Hz, 2H, bpy-H), 8.15–8.03 (m, 4H, bpy-H + phen-H), 7.87 (dd, J = 8.5 Hz, 2H, phen-H) 7.82 (d, J = 5.2 Hz, 2H, bpy-H), 7.61–7.50 (m, 4H, bpy-H + bpy-H), 7.33 (t, J = 6.4 Hz, 2H, bpy-H), see Figure S2. The <sup>1</sup>H NMR spectrum is similar to that reported elsewhere.<sup>S2</sup> Elemental analysis data for C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>Cl<sub>2</sub>Ru × H<sub>2</sub>O (%): calculated C 56.31, H 3.84, N 12.31; found C 56.28, H 3.82, N 12.29. Maxima λ<sub>max</sub> (nm) of the UV-VIS spectra in the aqueous phase (and the corresponding molar extinction coefficients in units M<sup>-1</sup>·cm<sup>-1</sup>): 264 (47800), 286 (52900), 450 (14200). The UV-VIS spectrum of Ru(bpy)<sub>2</sub>(phen) is exhibited in Figure S3.

## 2. BZ droplets

To prepare BZ droplets, a 50 µl aliquot of the solution containing malonic acid (0.36 M), NaBrO<sub>3</sub> (0.27 M), NaBr (0.07 M), Ru(bpy)<sub>2</sub>(phen) (3 mM), and H<sub>2</sub>SO<sub>4</sub> (1.2 M) is dispersed in fluorinated oil (FC-40 with 2% (w/w) surfactant Pico-Surf<sup>TM</sup>1, 500 µl) by shaking.

## 3. Experimental Setup

The block scheme of our experimental setup is exhibited in **Figure S6**. Oscillations of the BZ droplets or the other pieces of BZ gels immersed in the CFBZ solution (catalyst free BZ solution) are observed under a microscope (Zeiss Stemi-2000) equipped with a black-white CCD camera (QImaging Retiga 2000R) connected to a personal computer. A Petri dish with the BZ droplets (pieces of gels) is illuminated from below with a LED light source through an interference filter with the wavelength of the maximum transmission at λ = 450 nm. Analyzing light does not affect the BZ oscillations. Recording kinetic curves in selected spatial points (pixels) and geometrical measurements of the BZ microspheres are performed using software QCapture Pro.

In the case of the droplets or the pieces of the gels, the space-time plot is built along specified lines. The pixels along the specified lines are stored at the regular time intervals equal to 1 s. The stored pixel lines are sequentially lined up as a function of time on a computer. This procedure leads to the construction of a space-time plot.

## 4. Catalyst synthesis. Part II

*Synthesis of bis(2,2'-bipyridine)(5-acrylamido-1,10-phenanthroline) ruthenium(II) dichloride, Ru(bpy)<sub>2</sub>(5-acphen).* Bis(2,2'-bipyridine)ruthenium(II) dichloride (200.0 mg, 0.413 mmol) and 5-acrylamido-1,10-phenanthroline (123.6 mg, 0.496 mmol) are mixed in ethanol (10 ml). The mixture is kept stirring at 70 °C for 11 h. The reaction mixture is then cooled and filtered, the filtrate is evaporated in vacuum. The residue is dissolved in H<sub>2</sub>O (5 ml), and unreacted compounds are extracted 2 times with ethyl acetate (2×10 ml) and 2 times with CH<sub>2</sub>Cl<sub>2</sub> (2×10 ml). The water solution is evaporated to leave Ru(bpy)<sub>2</sub>(5-acphen) (206.0 mg, 0.281 mmol) as a red powder, yield 68%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 10.86 (s, 1H, NH), 9.03 (d, J = 8.4 Hz, 1H, phen-H), 8.9-8.79 (m, 4H, phen-H), 8.77 (s, 1H, phen-H), 8.74 (d, J = 8.0 Hz, 1H, phen-H), 8.20 (t, J = 8.0 Hz, 2H, bpy-H), 8.15 (d, J = 7.2 Hz, 1H, bpy-H), 8.09 (td, J = 7.7 Hz, J = 2.8 Hz, 2H, bpy-H), 8.02 (dd, 1H, J = 5.2 Hz, bpy-H), 7.90 (m, 1H, bpy-H), 7.81 (t, J = 6.6 Hz, 3H, bpy-H), 7.56 (d, J = 5.2 Hz, 4H, bpy-H), 7.35 (t, J = 6.6 Hz, 2H, bpy-H), 6.89 (dd, J = 16.5 Hz, J = 10.2 Hz, 1H, CH=CH<sub>2</sub>), 6.40 (d, J = 16.8 Hz, 1H, CH=CH<sub>2</sub>), 5.92 (d, J = 11.6 Hz, 1H, CH=CH<sub>2</sub>). The <sup>1</sup>H NMR image is shown in Figure S4. Elemental analysis data for C<sub>35</sub>H<sub>27</sub>N<sub>7</sub>Cl<sub>2</sub>ORu × H<sub>2</sub>O (%): calculated C 55.93, H 3.89, N 13.04; found C 55.90, H 3.91, N 12.97. Maxima λ<sub>max</sub> (nm) of the UV-VIS spectra in the aqueous phase (and the corresponding molar extinction coefficients in units M<sup>-1</sup>·cm<sup>-1</sup>) are 285 (50700), 451(12500). The UV-VIS spectrum is exhibited in Figure S5.

## 5. Synthesis of gels. Part I

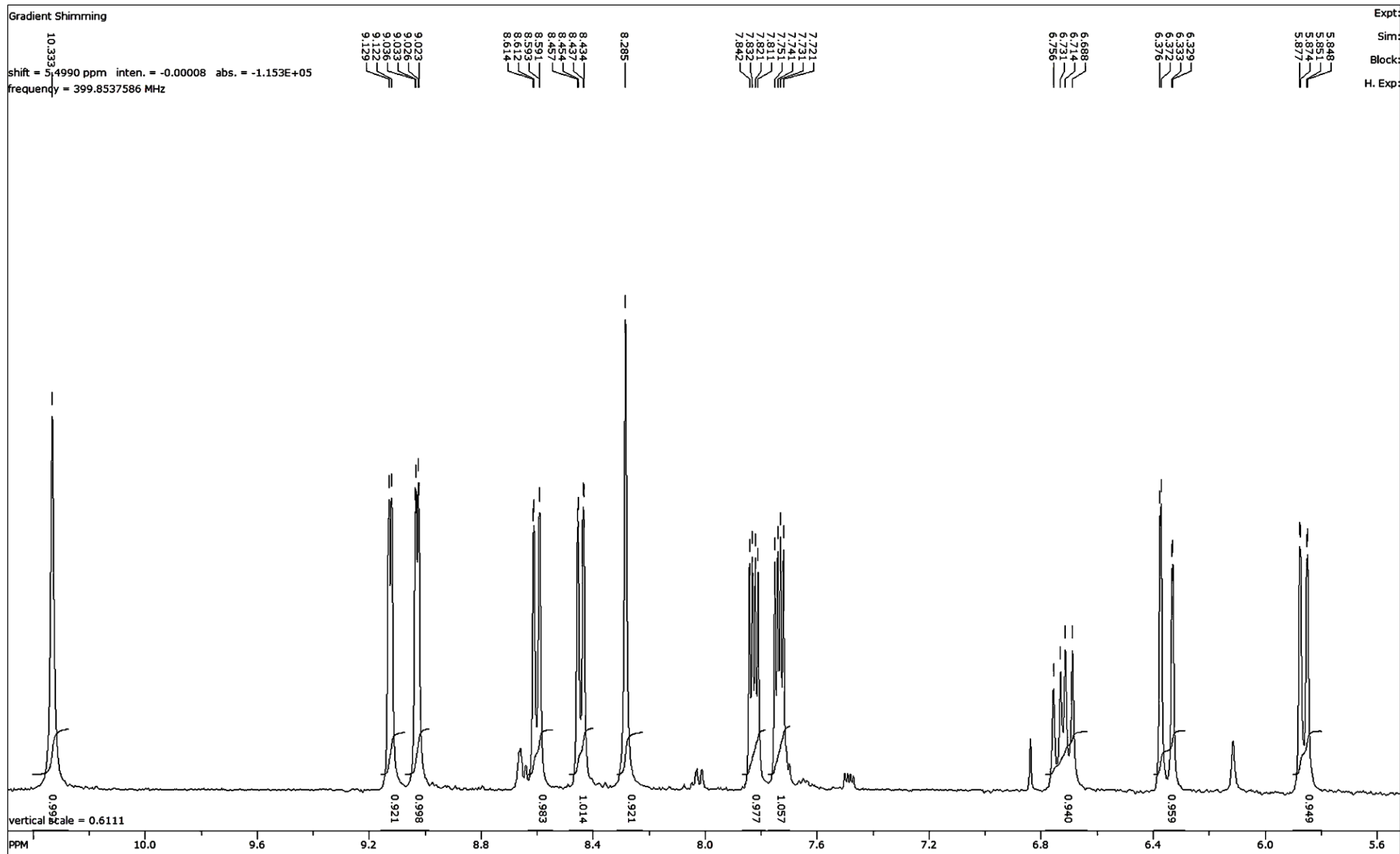
To synthesize gel **1**, first, *N*-isopropylacrylamide (NIPA) (Aldrich, analytical grade, 78.1 mg, 0.690 mmol), Ru(bpy)<sub>2</sub>(5-acphen) (7.3 mg, 0.010 mmol), 2% *N,N*-methylenebisacrylamide (MBA, Aldrich, analytical grade, 1.1 mg, 0.007 mmol) in water (53 μl), and 20% ammonium persulfate (APS, Aldrich, analytical grade, 7.9 mg, 0.035 mmol) in water (39.4 μl) are mixed together. Distilled water is added to the resulting mixture to reach a total volume of 466 μl, and a homogeneous solution is obtained. The mixture is degassed under vacuum and heated to 65 °C. To start polymerization, 20% tetramethylethylenediamine (TMEDA, Aldrich, analytical grade, 6.8 mg, 0.059 mmol) in water (34 μl) is added. The final mixture is carefully stirred and dispersed in fluorinated oil (FC-40 with 2% (w/w) surfactant Pico-Surf™1 from Dolomite Microfluidics, 2 ml) by shaking for 3 seconds. The dispersion obtained is heated at 65 °C for 60 min and kept at room temperature for 15 hours. Fluorinated oil is removed by decantation, and the resulting pieces of gel **1** (in the form of microspheres) are incubated 3 times for 1 day in distilled water (10 ml) to remove unreacted monomers. About 50% of the catalyst Ru(bpy)<sub>2</sub>(5-acphen) is unreacted, which was estimated from its concentration in wash water.

## 6. Synthesis of gels. Part II

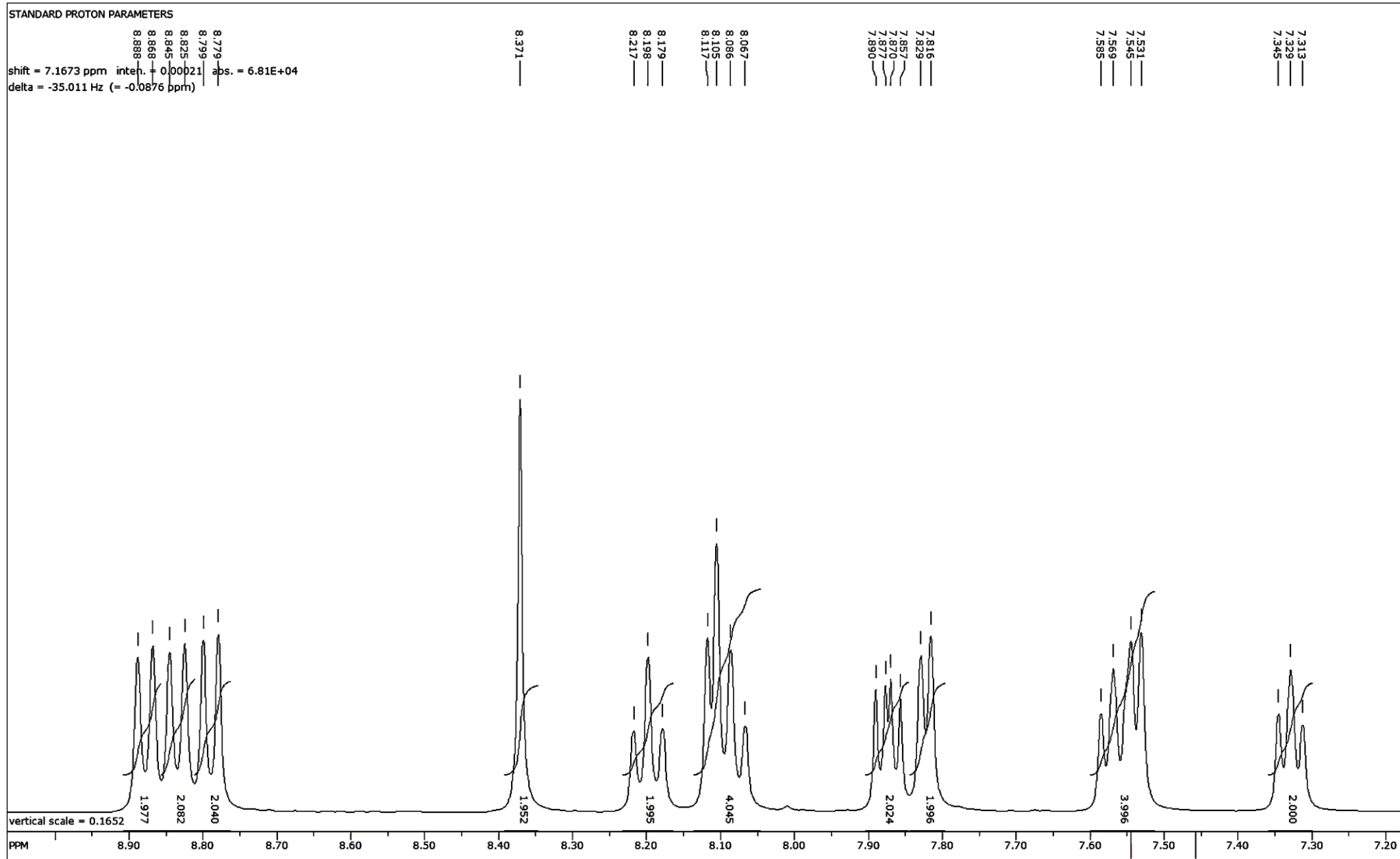
To synthesize gels **2a-c**, we mixed together 3 M *N*-isopropylacrylamide (NIPA, 78.1 mg, 0.690 mmol) in DMSO (230  $\mu$ l), 2% *N,N*-methylenebisacrylamide (MBA, 1.1 mg, 0.007 mmol) in water (53  $\mu$ l), 10% 2-acrylamide-2-methylpropanesulfonic acid (AMPS, Aldrich, analytical grade, 4.3 mg, 0.021 mmol) in water (42.9  $\mu$ l), 20% ammonium persulfate (APS, 7.9 mg, 0.035 mmol) in water (39.4  $\mu$ l), DMSO (Aldrich, analytical grade, 20  $\mu$ l) and Ru(bpy)<sub>2</sub>(5-acphen). Amount of Ru(bpy)<sub>2</sub>(5-acphen) was 7.3 mg (0.010 mmol) in the case of gel **2a**, 11 mg (0.015 mmol) in the case of gel **2b**, or 14.7 mg (0.020 mmol) in the case of gel **2c**. Water is added to the resulting mixtures until the total volume of 466  $\mu$ l is obtained. The resulting mixtures were homogeneous. The mixture is degassed under vacuum and heated to 65 °C. To start polymerization, 20% tetramethylethylenediamine (TMEDA, 6.8 mg, 0.059 mmol) in water (34  $\mu$ l) is added. Further processing of the reaction mixtures for obtaining gels is carried out as in the case of gel **1**. About 50% percent of Ru (bpy)<sub>2</sub>(5-acphen) is unreacted, which is estimated from its concentration in wash water.

## References

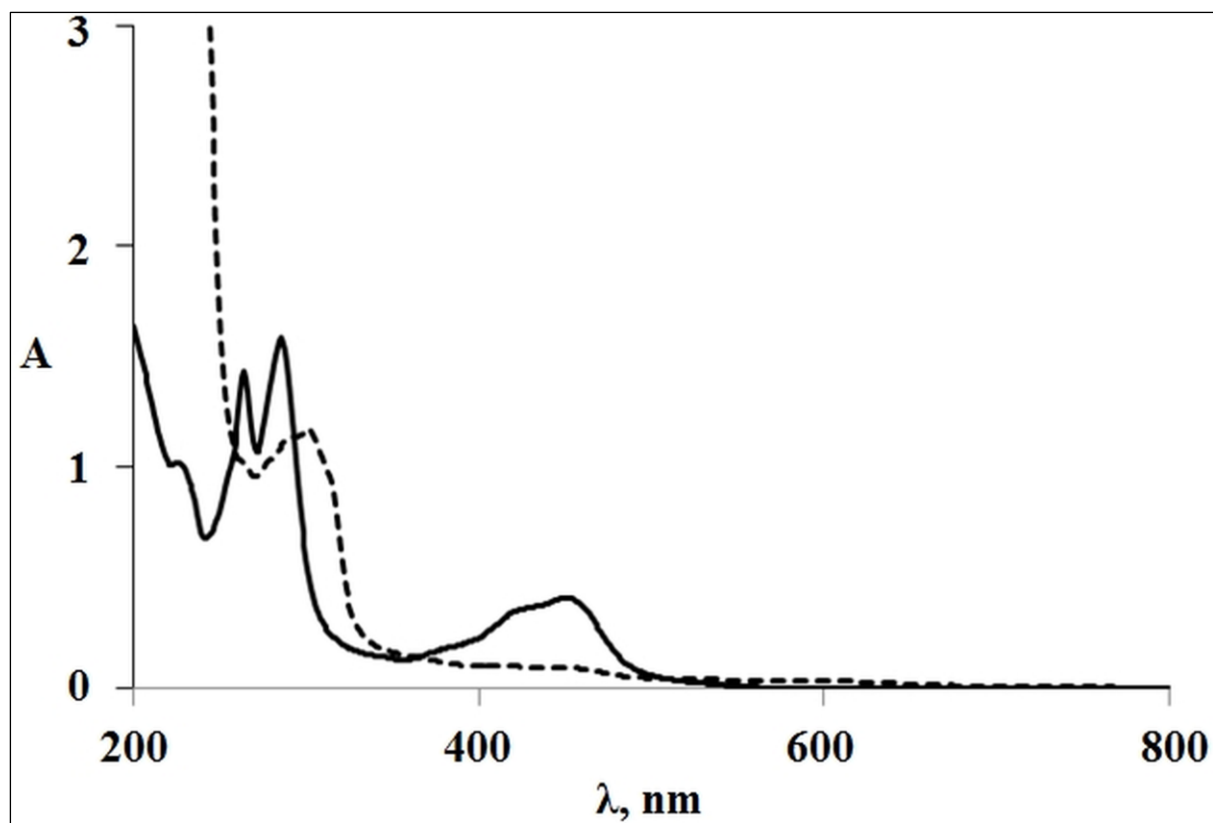
- [S1] T. Arimura and M. Mukaia, *Chem. Commun.*, 2014, **50**, 5861.  
[S2] X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1995, **34**, 5791.



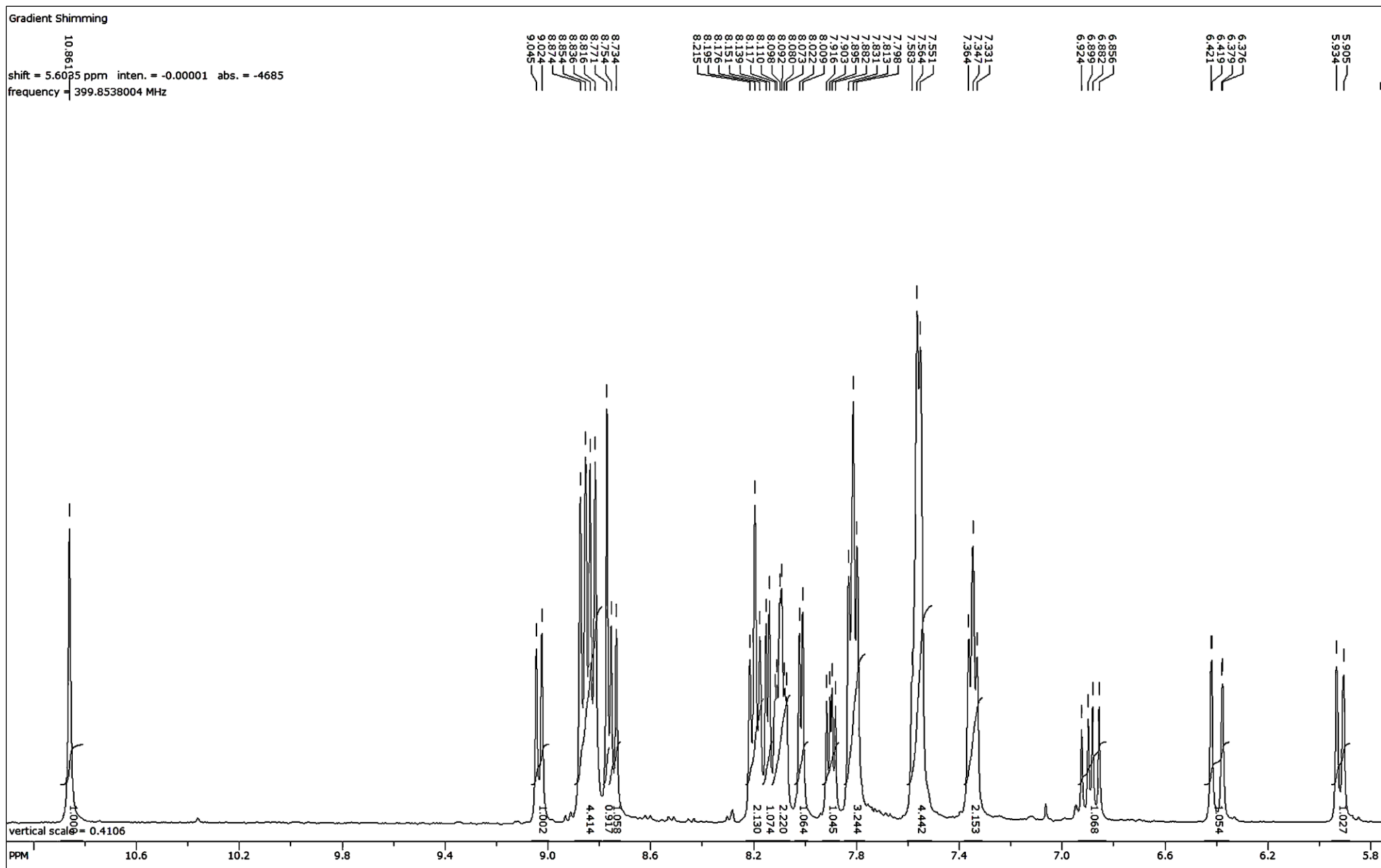
**Figure S1.**  $^1\text{H}$  NMR spectrum of 5-acrylamido-1,10-phenanthroline.



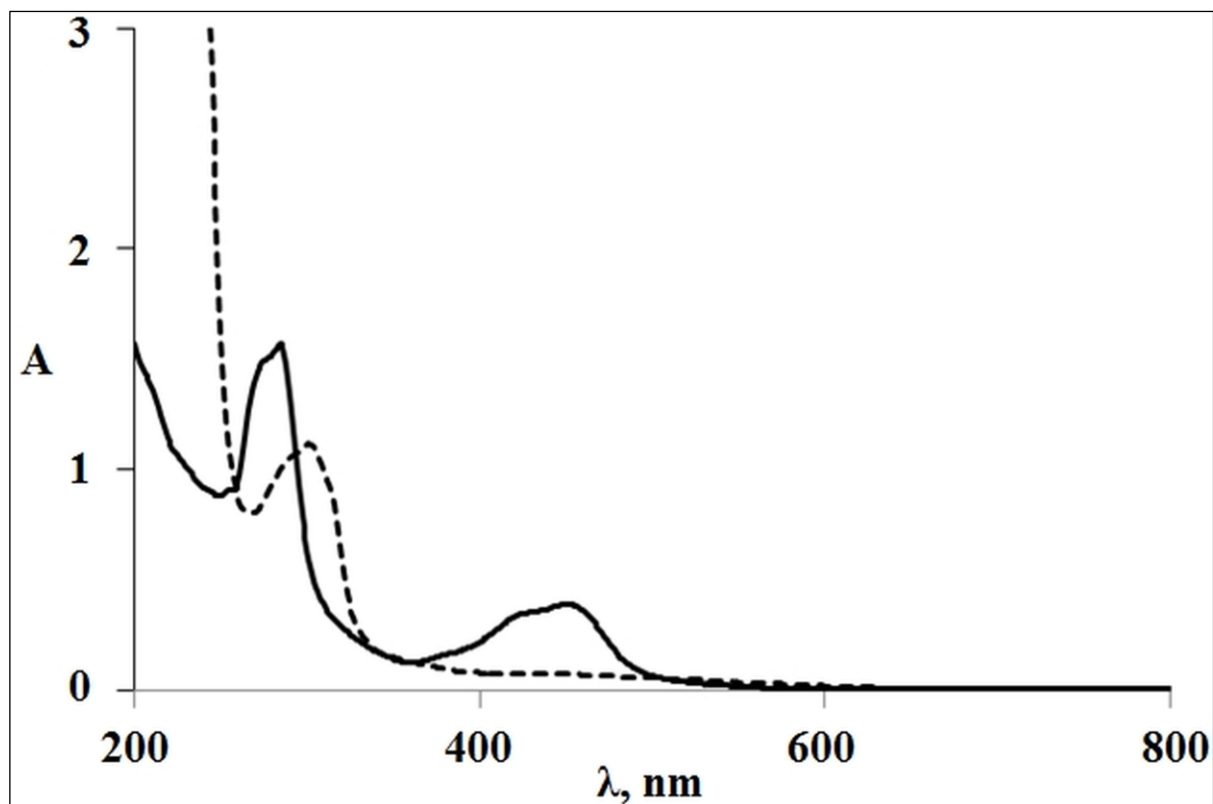
**Figure S2.**  $^1\text{H}$  NMR spectrum of bis(2,2'- bipyridine)(1,10-phenanthroline) ruthenium (II) dichloride,  $\text{Ru}(\text{bpy})_2(\text{phen})$ .



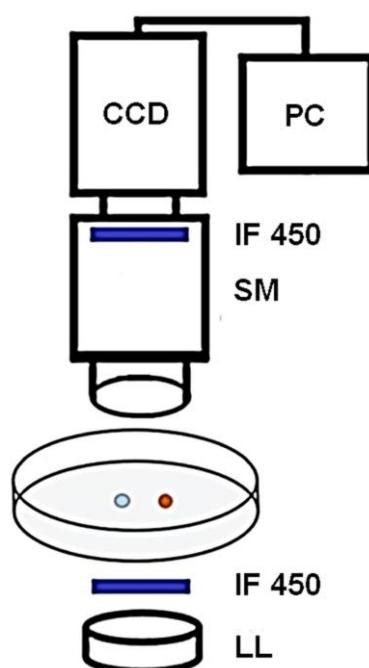
**Figure S3.** UV-VIS spectra of bis(2,2'- bipyridine)(1,10-phenanthroline)ruthenium dichloride in reduced (II) (solid line) and oxidized (III) (dotted line) states.  $[\text{Ru}(\text{bpy})_2(\text{phen})] = 3.33 \times 10^{-5} \text{ M}$ .



**Figure S4**  $^1\text{H}$  NMR spectrum of bis(2,2'-bipyridine)(5-acrylamido-1,10-phenanthroline)ruthenium (II) dichloride,  $[\text{Ru}(\text{bpy})_2(5\text{-acphen})]$ .



**Figure S5.** UV-VIS spectra of bis(2,2'-bipyridine)(5-acrylamido-1,10-phenanthroline)ruthenium dichloride, Ru(bpy)<sub>2</sub>(5-acphen), in reduced (solid line) and oxidized (dotted line) states. [Ru(bpy)<sub>2</sub>(5-acphen)] =  $3.33 \times 10^{-5}$  M.



**Figure S6.** Experimental Setup. The block scheme of the experimental setup for recording the BZ oscillations in BZ droplets and small BZ pieces of the gels. Designations: SM, stereo microscope (Zeiss Stemi-2000); CCD, a CCD video-camera (QImaging Retiga 2000R); PC, personal computer; IF 450, interference filters with the wavelength of the maximum transmission at  $\lambda = 450$  nm; LL, analysing LED light.



**Figure S7.** Ball of gel 2b.

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