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Fe(bathophen)$_2$(phen)-based self-oscillating gel driven by the Belousov–Zhabotinsky reaction

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1. Materials and methods

For the synthesis, we have used the following chemicals (all from Aldrich, analytical grade) without further purification: acryloyl chloride, 1,10-phenanthroline-5-amine, bathophenanthroline, N-isopropylacrylamide, N,N'-methylenebisacrylamide, iron(II) sulfate heptahydrate, ammonium persulfate, tetrahydrofuran, benzene, ethyl acetate, ethanol, isopropanol, methylene chloride, tetramethylethylenediamine, as well as distilled water. Column chromatography was performed using Merck silica gel 60 as a sorbent. ^{1}H NMR spectra of the obtained substances are recorded on a Bruker Avance III 400 MHz at temperature 23 ºC in the Fourier transform mode with the chemical shifts being reported in ppm downfield from tetramethylsilane (TMS).

The following abbreviations are used to describe ^{1}H NMR spectra: δ = 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 have used $(CD_3)_2SO$. UV-visible absorption spectra are measured on a UV-3100 spectrophotometer. Elemental analysis is done using microanalysis methods (elemental analyzer Perkin Elmer 2400, accuracy 0.4%).

2. Catalyst synthesis

The ligand 5-acrylamide-1,10-phenanthroline is synthesized as described earlier.[S1] In this synthesis, 1,10-phenanthroline-5-amine (58.6 mg = 0.300 mmol) is added to a solution of tetramethylethylenediamine (29.9 μL, 23.2 mg = 0.200 mmol) in 9 mL of dry tetrahydrofuran. The suspension is stirred for 1 h at 10 °C. Then a solution of acryloyl chloride (28.5 μL, 31.9 mg = 0.352 mmol) in 1 mL of tetrahydrofuran is slowly added at 10 °C. The mixture obtained is kept stirring for 20 h at 10 °C. Then, the solvent was evaporated. Purification by column chromatography on silica gel (ethanol/methylene chloride = 1:7) gives 5-acrylamide-1,10-phenanthroline (37.0 mg = 0.148 mmol) in the form yellow powder. The yield was about 49%.

Parameters of the ^{1}H NMR spectra in deuterated dimethyl sulfoxide $(CD_3)_2SO$ are as follows: δ 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, $CH=CH_2$), 6.35 (d, J = 16.8 Hz, 1H, $CH=CH_2$), 5.86 (d, J = 10.4 Hz, 1H, $CH=CH_2$). Elemental analysis data for $C_{15}H_{11}N_3O$ (%): calculated C 72.28, H 4.45, N 16.86; found C 72.31, H 4.50, N 16.83. The coincidence of the calculated and found data is quite good. The parameters of the ^{1}H NMR spectra are similar to the parameters reported earlier.[S1]

To synthesize a derivative of the catalyst Fe(bathophen)$_2$(phen), which is able to be copolymerized with N-isopropylacrylamide, we have synthesized bis(bathophenanthroline)(5-acrylamido-1,10-phenanthroline)Fe(II) sulfate [= Fe(bathophen)$_2$(acphen)] **1** containing acrylamide fragment in the phenanthroline ligand. For this synthesis, bathophenantroline (66.5 mg = 0.2 mmol) and 5-acrylamide-1,10-phenanthroline (24.9 mg = 0.1 mmol) were mixed in 10 mL of isopropanol. To the resulting mixture was added with stirring 1 ml of 0.1 M solution of iron(II) sulfate (28.8 mg = 0.1 mmol). The mixture was kept stirring for 1 h. Then, the reaction mixture was evaporated in vacuum. The residue was dissolved in 5 mL of H_2O and unreacted compounds have been extracted 2 times with 5 ml of benzene and 2 times with 5 ml of tetrahydrofuran. Water solution was evaporated to give Fe(bathophen)$_2$(acphen) **1** (85.0 mg = 0.8 mmol) as a red powder with the 80% yield, mp > 300 °C.

The data of elemental analysis confirmed that we have synthesized Fe(bathophen)$_2$(acphen) **1**. Elemental analysis data for $C_{63}H_{43}N_7O_5SFe$ (%): calculated C 70.98, H 4.07, N 9.20; found C 71.15, H 4.04, N 9.09. Maxima λ_{max} (nm) of the UV-VIS spectra in the aqueous phase (and the corresponding molar extinction coefficients in units $M^{-1}\cdot cm^{-1}$) are 281 (112500), 526(18000). The UV-VIS spectrum of Fe(bathophen)$_2$(acphen) **1** is exhibited in **Figure S1**.

3. Synthesis of gels

To synthesis gels, we have mixed together 230 μL of 3 M N-isopropylacrylamide (IPA) (78.1 mg = 0.690 mmol) in dimethyl sulfoxide (DMSO), 34.5 μL of 200 mM, N,N'-methylenebisacrylamide (MBA) (1.1 mg = 0.007 mmol) in water, 20 μL of DMSO and 16.0 mg (= 0.015 mmol) of Fe(bathophen)$_2$(acphen) in the case of gel **2**, or 10.7 mg (=0.01 mmol) of Fe(bathophen)$_2$(acphen) in the case of gel **3**, or 21.3 mg (= 0.020 mmol) of Fe(bathophen)$_2$(acphen) in the case of gel **4**, or 26.7 mg (= 0.025 mmol) of Fe(bathophen)$_2$(acphen) in the case of gel **5**. Water was added to the resulting mixture until the total volume of 466 μL was obtained. The mixture was degassed under vacuum and heated to 70 °C. To start polymerization, 34 μL of 1 M ammonium persulfate (APS) (7.9 mg = 0.035 mmol) in water was added. The mixture obtained was heated at 70 °C for 3 h and kept for 15 hours at room temperature. The resulting pieces of gels were incubated 3 times for 1 day in 10 mL of distilled water to remove unreacted monomers. About 65% of the catalyst Fe(bathophen)$_2$(acphen) was unreacted, which was estimated from its concentration in wash water. The amount (N, mmol) of the catalyst inside the gel was estimated as the difference between the amount of the catalyst loaded and the amount of the catalyst washed out during the soaking of the gel ($N_{inside} = N_{loaded} - N_{washed\ out}$). The amount of the catalyst washed out was estimated spectrophotometrically ($N_{washed\ out}$ =

$C_{\text{washed out}} \times V_{\text{washed out}}$; $C_{\text{washed out}} = A_{\text{catalyst}}/\varepsilon_{\text{catalyst}}$). Since the gel periodically changed dimensions (volume), the amount of the catalyst inside the gel was referred to the amount of IPA ($\text{mol\%}_{\text{catalyst}} = N_{\text{catalyst}}/N_{\text{IPA}}$) and not to the volume of the gel.

4. Experimental Setup

The block scheme of our experimental setup is exhibited in **Figure S2**. Oscillations of the pieces of BZ gels immersed in the CFBZ solution (= catalyst free BZ solution) were observed using microscope (Zeiss Stemi-2000) equipped with a black-white CCD camera (QImaging Retiga 2000R) connected to a personal computer. A Petri dish with the pieces of the gels was illuminated from below with a LED light source through an interference filter with the wavelength of the maximum transmission at $\lambda = 525$ nm. Recording of light transmission through the pieces of the gels and geometrical measurements of the pieces of the gels have been performed using software QCapture Pro.[S2] A precise stage micrometer was used to calibrate microscope and QCapture Pro for precise measurement.

For each piece of the gel, the space-time plot was constructed for cross-sections indicated by white arrows (see Figure 1). The cross-sections through the stack of the pictures were made to reduce the dimensionality into one spatial dimension and time. The sequence of the cross-sections (recorded every second) in time was combined together to create a space–time plot for analysis of the linear dimensions and the periods of the oscillations. We used the software Plotto to create the space-time plots.[S3] The attached piece of the gel was obtained by sticking one of the surfaces of the piece onto a rough surface of the glass. The partially attached piece of the gel was obtained by attaching a branch extending from the piece to a notch in the glass.

References

S1. I. L. Mallphanov and V. K. Vanag, *Mendeleev Commun.*, 2022, **32**, 4, 507.

S2. Q-Capture Pro 7, https://www.photometrics.com/

S3. P. S. Smelov, *Plotto: Space-time plotter [Computer software]*, 2016, https://github.com/x3mer/plotto

Figures.

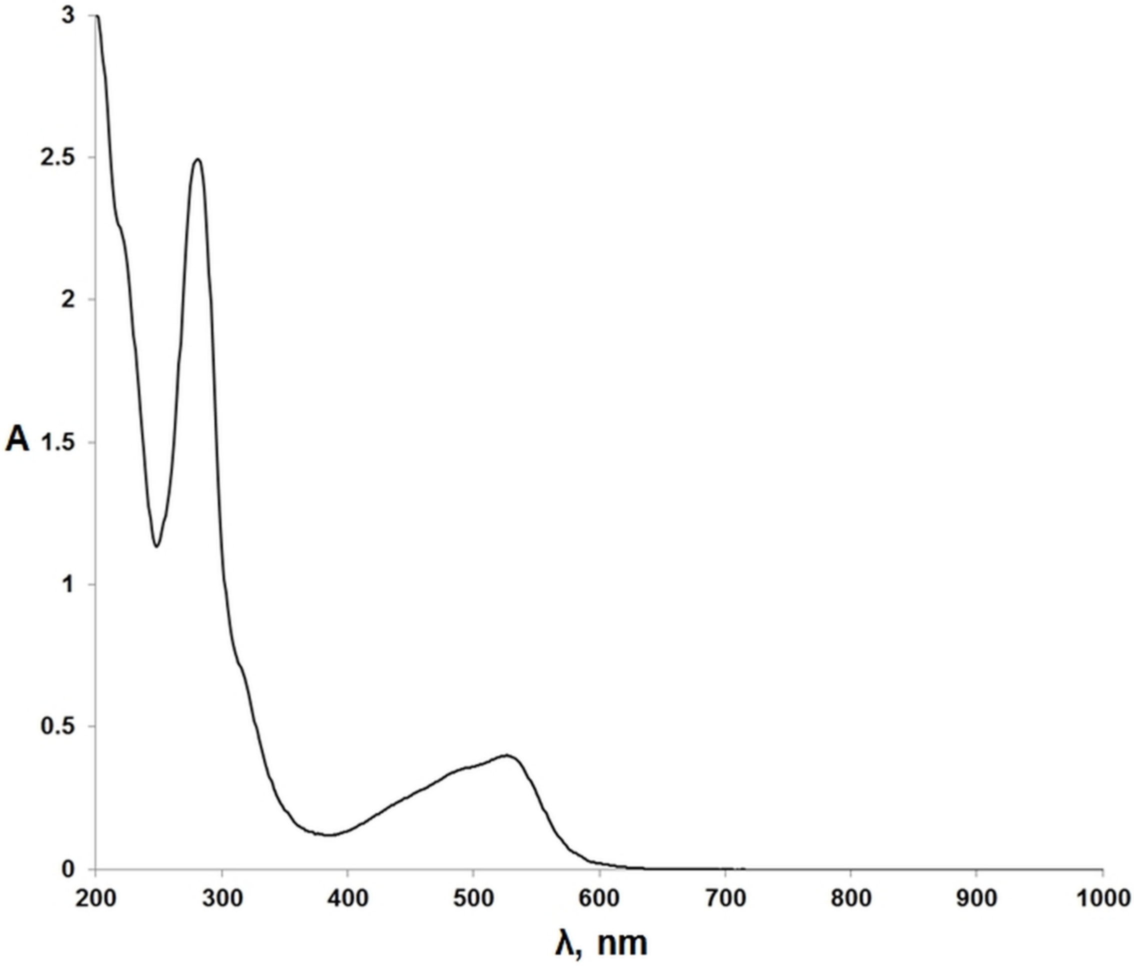

Figure S1. UV-VIS spectrum of bis(bathophenanthroline)(5-acrylamido-1,10-phenanthroline)iron(II) sulfate **1**. C = 2.2 × 10^{-5} M.

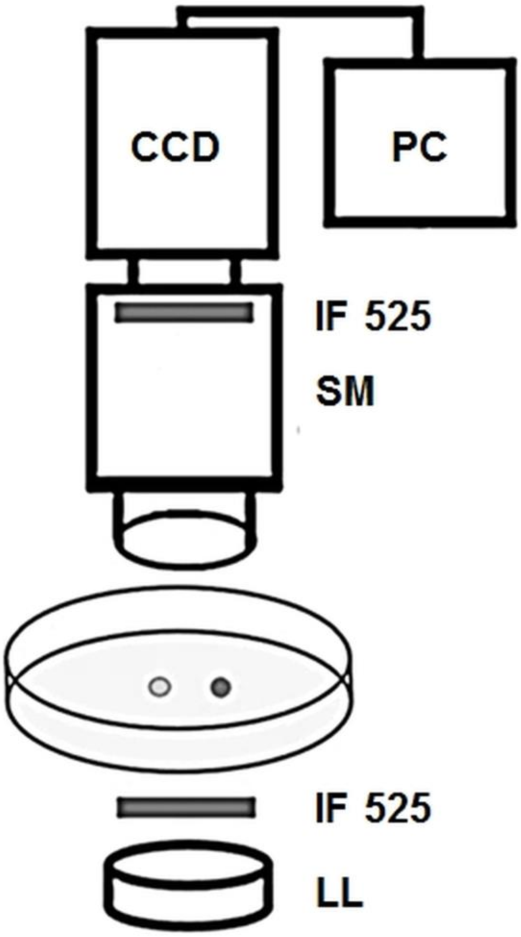

Figure S2. Experimental Setup. The block scheme of the experimental setup for recording the oscillations of the pieces of the gels. Designations: SM, stereo microscope (Zeiss Stemi-2000); CCD, a CCD video-camera (QImaging Retiga 2000R); PC, personal computer; IF 525, interference filters with the wavelength of the maximum transmission at λ = 525 nm; LL, analysing LED light.

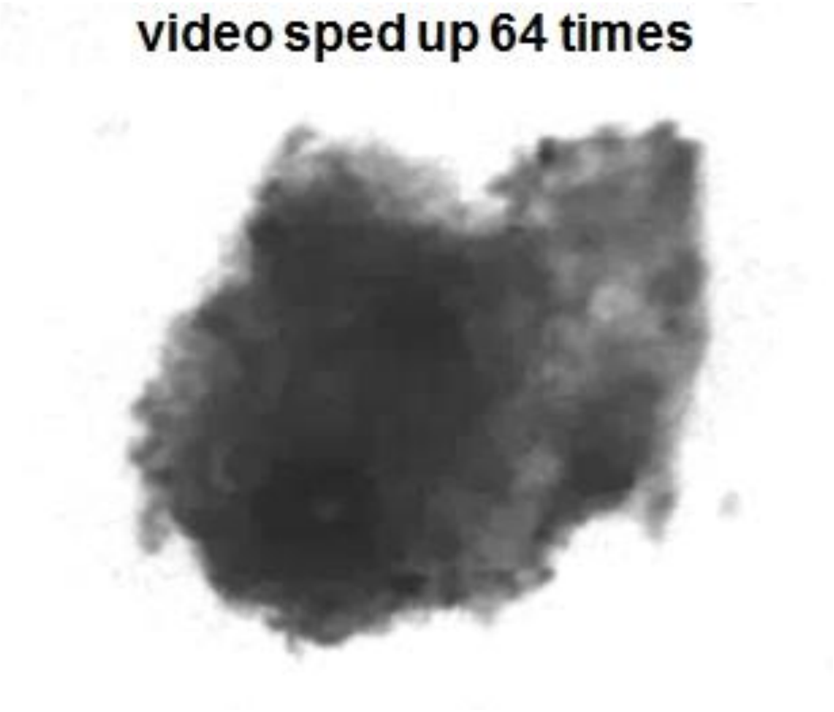

Figure S3. Attached piece of gel **2**.

Click on image to play a movie

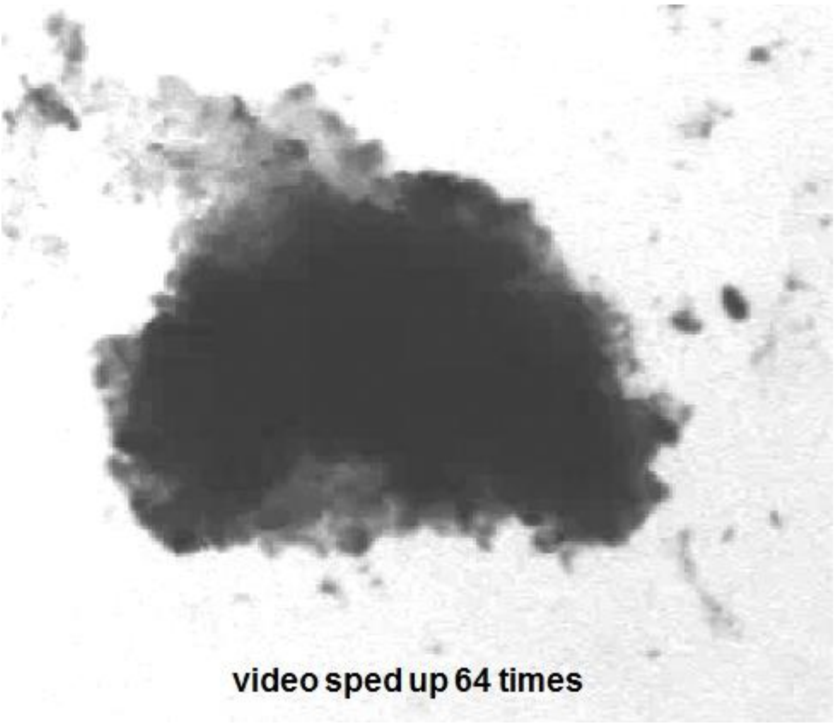

Figure S4. Partially attached piece of gel **2**.

Click on image to play a movie