Supplementary Information for

"Anisotropically Self-oscillating Gels by Spatially

Patterned Interpenetrating Network"

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1. Experimental Procedures

1.1. Fabrication of spatially patterned self-oscillating gels



Fig. S1 Schematic for fabricating the base gel. Figure made in Biorender.



Fig. S2 Schematic illustration describing analyzed regions. (a) Horizontal and vertical as analyzed in the main text. (b) IPN regions as analyzed in the ESI. Figure made in Biorender.

1.2. Equilibrium swelling ratio test

The equilibrium swelling ratio was calculated by **eqn (S1)** with the measured gel lengths. Then, the discrete ratio data were fitted to the Boltzmann sigmoidal equation (**eqn (S2)**), as this equation can be exploited as a tracking tool of the volume phase transition of the NIPAAm-based smart gels.¹

$$Equilibrium Swelling Ratio (-) = \frac{\text{Length}(\text{Redox state})(T)}{\text{Length}(\text{Oxidation state})(T(\text{initial}))} eqn (S1)$$

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0)/dx}} + A_2$$
 eqn (S2)

2. Supporting Figures and notes

dx

 \mathbb{R}^2

Adj. R²

2.1. Equilibrium swelling ratio fitting parameters

4.00214

0.99810

0.99621

Table S1. Parameters resulting fitting the Boltzmann sigmoidal equation to ESR values. Each sample is abbreviated as described in **2.5** of the main text. (OXI) indicates the oxidized state $(Ru(bpy)_3^{3+})$ while (RED) indicates the reduced state $(Ru(bpy)_3^{2+})$. Horizontal is (1) and vertical is (2) as described in **Fig. S2(a)**.

	SOG/P-IPN(0.05M)					
Parameter	Horizontal		Vertical			
	OXI	RED	OXI	RED		
A ₁	1.06419	1.11049	1.06531	1.10384		
A ₂	0.64076	0.63416	0.65385	0.63839		
X 0	22.30641	17.80178	20.88645	16.81241		
dx	5.59327	6.13972	5.00097	5.23307		
R ²	0.99327	0.99995	0.99400	0.99963		
Adj. R ²	0.98655	0.99987	0.98873	0.99925		
		SOG/P-IP	N(0.05M)			
Parameter	Horizontal		Vertical			
	OXI	RED	OXI	RED		
A ₁	1.02574	1.05373	1.09237	1.40905		
A ₂	0.76945	0.74364	0.64472	0.60534		
Xo	21.20213	17.57168	20.01525	11.22981		

4.13361

0.99924

0.99849

5.95783

0.99999

0.99901

7.12770

0.99967

0.99933

	SOG/P-IPN(0.05M)					
Parameter	Horizontal		Vertical			
	ΟΧΙ	RED	OXI	RED		
A ₁	1.02326	1.04067	1.02285	1.04489		
A ₂	0.82776	0.80950	0.65330	0.62628		
x ₀	20.64059	17.01876	23.16028	19.59075		
dx	4.43269	4.93873	3.89371	4.76017		
R ²	0.99789	0.99810	0.99900	0.99891		
Adj. R ²	0.99579	0.99621	0.99726	0.99728		

2.2. Equilibrium swelling ratio test



Fig. S3 Representative equilibrium swelling ratio (ESR) Data (horizontal is 1) and vertical is 2) as described in **Fig. S2(b)**). (a) SOG/P-IPN(0.05M) horizontal, (b) SOG/P-IPN(0.05M) vertical, (c) SOG/P-IPN(0.25M) horizontal, (d) SOG/P-IPN(0.25M) vertical, (e) SOG/P-IPN(6M) horizontal, and (f) SOG/P-IPN(6M) vertical . (n=3 for each group). The gels were immersed in the BZ substrate solution containing [HNO₃] = 894 mM and [NaBrO₃] = 84 mM for the oxidized state, and in [HNO₃] = 894 mM, [NaCl] = 84 mM, and [MA] = 64 mM for the reduced state. NaCl was added to maintain the ionic strength.



Fig. S4 Representative equilibrium swelling ratio (ESR) data of the horizontal direction in the AA-IPN regions (Left IPN Horizontal is ③ and Right IPN Horizontal is ④ as described in **Fig. S2(b)**): (a) SOG/P-IPN(0.05M) left IPN horizontal, (b) SOG/P-IPN(0.05M) right IPN horizontal, (c) SOG/P-IPN(0.25M) left IPN horizontal, (d) SOG/P-IPN(0.25M) right IPN horizontal, (e) SOG/P-IPN(6M) left IPN horizontal, and (f) SOG/P-IPN(6M) right IPN horizontal. (*n=3* for each group). The gels were immersed in the BZ substrate solution containing [HNO₃] = 894 mM and [NaBrO₃] = 84 mM for the oxidized state, and in [HNO₃] = 894 mM, [NaCl] = 84 mM, and [MA] = 64 mM for the reduced state. NaCl was added to maintain the ionic strength.



Fig. S5 Representative equilibrium swelling ratio (ESR) data of the vertical direction in the AA-IPN regions (Left IPN Vertical is (5) and Right IPN Vertical is (6) as described in **Fig. S2**): (a) SOG/P-IPN(0.05M) left IPN vertical, (b) SOG/P-IPN(0.05M) right IPN vertical, (c) SOG/P-IPN(0.25M) left IPN vertical, (d) SOG/P-IPN(0.25M) right IPN vertical, (e) SOG/P-IPN(6M) left IPN vertical, and (f) SOG/P-IPN(6M) right IPN vertical. (*n=3* for each group). The gels were immersed in the BZ substrate solution containing [HNO₃] = 894 mM and [NaBrO₃] = 84 mM for the oxidized state, and in [HNO₃] = 894 mM

In **Fig. S4** and **S5**, the IPN region of SOG/P-IPN(6M) did not appear to have any difference in size between the oxidized or reduced states. The graphs of the AA-IPN regions of SOG/P-IPN(0.25M) and SOG/P-IPN(0.05M) seemed to have a smaller difference in size than their respective base gel (vertical 2)) regions, with SOG/P-IPN(0.05M) having an AA-IPN region ESR redox-amplitude the most similar to the base region.

2.3. Calculation of the period and the amplitude during the BZ reaction

The gel-size time profile during the BZ reaction was plotted using ImageJ (NIH, USA). All gels were analyzed after 10,000 seconds in the BZ solution. The length of each gel in each of the directions was normalized to the minimum value of the same gel in the same direction (**eqn (S3)**). The period and the amplitude were quantitatively calculated by **eqn (S4)** and **(S5)** respectively from the analyzed length-time profiles with parameters, as described in **Fig. S6**. Vertical and horizontal amplitude values are described in the main text (**Fig. 4**), while left and right IPN values are described in **Fig. S7**.

$$Length(-) = \frac{Length_t}{Length_{minumum}} eqn (S3)$$

$$Period [s] = Time(pre) - Time(post)$$
 eqn (S4)

$$Amplitude [-] = Length(top) - Length(bottom) eqn (S5)$$



Fig. S6 Calculation of period and amplitude during the BZ reaction. This sample graph shows representative data taken from a vertical region of a 0.25 M gel (the same as in **Fig 1(c)**). The substrate solution for self-oscillation contains $[HNO_3] = 894$ mM, $[NaBrO_3] = 84$ mM, and [MA] = 64 mM.

Table S2. Period and amplitude of the horizontal and vertical directions of the gels. The amplitude ratio is calcul	lated
by dividing the horizontal amplitude of each gel by the vertical amplitude of the same gel.	

Gel	Period (s)		Normalized amplitude (-) (x10 ⁻²)		Amplitude ratio (-)
	Horizontal	Vertical	Horizontal	Vertical	(Horizontal/ Vertical)
SOG/P- IPN(0.05M)	1610 ± 216	1616 ± 197	1.44 ± 0.54	1.71 ± 0.61	0.841 ± 0.057
SOG/P- IPN(0.25M)	1442 ± 477	1443 ± 504	0.91 ± 0.28	1.33 ± 0.45	0.691 ± 0.056
SOG/P- IPN(6M)	1888 ± 625	1887 ± 622	0.68 ± 0.28	1.58 ± 0.71	0.443 ± 0.060

2.4. Detailed graphs displaying different amplitudes of oscillation in different directions in the gel.

The amplitude ratio was used to compare the amplitude of the IPN regions to that of the vertical region (**eqn (S6)**). This ratio ($R_{OSC-ESR}$) was calculated as the average of the amplitudes of the two IPN regions ($A_{OSC-RIPN}$ for the right IPN and $A_{OSC-LIPN}$ for the left IPN), divided by the amplitude of the vertical direction ($A_{OSC-ver}$) of the same gel (**eqn (S6**)):



Fig. S7 Time profiles of the gel length in the vertical AA-IPN regions ((5) and (6) as described in **Fig. S2(b)**) during self-oscillation during the BZ reaction at 20 °C. (a-f) Gel length time profiles for varying AA-IPN concentrations: (a) SOG/P-IPN(0.05M) right IPN, (b) SOG/P-IPN(0.05M) left IPN, (c) SOG/P-IPN(0.25M) right IPN, (d) SOG/P-IPN(0.25M) left IPN, (e) SOG/P-IPN(6M) right IPN, and (f) SOG/P-IPN(6M) left IPN. (g) Amplitude Ratio. (*n*=6 for each group). The substrate solution for self-oscillation contains [HNO₃] = 894 mM, [NaBrO₃] = 84 mM, and [MA] = 64 mM. Statistical analysis was performed by a Kruskal-Wallis ANOVA with a Dunn post-hoc test (**, p < 0.01).

In **Fig. S7**, the AA-IPN region of SOG/P-IPN(6M) does not appear to have any volumetric oscillation. The graphs of the AA-IPN regions of SOG/P-IPN(0.25M) and SOG/P-IPN(0.05M) seem to have a smaller oscillation their respective base gel regions (as measured by vertical (2)), with SOG/P-IPN(0.05M) having an AA-IPN region volumetric oscillation amplitude the most similar to the base gel region. In specific, the ratios of the AA-IPN region (averaged between the right IPN (5) and left IPN (6)) amplitude to base gel region (vertical (2)) amplitude was found to be 0.796 ± 0.057 and 0.650 ± 0.80 for the SOG/P-IPN(0.05M) and SOG/P-IPN(0.25M) gels respectively.



Fig. S8 Schematic illustration of anisotropic deformational behaviour in this study during the BZ reaction.



Fig. S9 Spatio-temporal plot of a SOG/P-IPN(6M) gel during the BZ reaction in (a) vertical direction, (b) horizontal direction, and (c) IPN region. The concentrations of substrates were 894 mM HNO₃, 84 mM NaBrO₃, and 64 mM MA.



Fig. S10 (a) Schematic illustration to analyse the amplitude ratio (horizontal amplitude/vertical amplitude) with various area of patterned AA region. The horizontal size (H) was identical to all gels. (b) Changes in amplitude ratio with various patterning ratio during the BZ reaction.

3. References

1. A. L. Navarro-Verdugo, F. M. Goycoolea, G. Romero-Meléndez, I. Higuera-Ciapara and W. Argüelles-Monal, *Soft Matter*, 2011, **7**, 5847–5853.