

Supplementary Information

Synthesis of Zeolitic Imidazolate Framework-8 using an Electric Field in a Gelled Medium

Norbert Német,^{a,b} Gábor Holló,^c Nadia Valletti,^d Szabolcs Farkas,^a Brigitta Dúzs,^e Ákos Kukovecz,^f Gábor Schusztér,^g István Szalai,^h Federico Rossi,^d István Lagzi^{a,i*}

^aDepartment of Physics, Institute of Physics, Budapest University of Technology and Economics, H-1111 Budafoki út 8, Budapest, Hungary

^bDepartment of Organic Chemistry and Technology, Budapest University of Technology and Economics, H-1111 Budafoki út 8, Budapest, Hungary

^cDepartment of Fundamental Microbiology, University of Lausanne, Biophore Building, 1015 Lausanne, Switzerland

^dDepartment of Physical Sciences, Earth and Environment, University of Siena, piazzetta Enzo Tiezzi 1, 53100 Siena, Italy

^eDepartment of Chemistry, University of Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

^fInterdisciplinary Excellence Center, Department of Applied and Environmental Chemistry, University of Szeged, H-6720, Rerrich Béla tér 1, Szeged, Hungary

^gDepartment of Physical Chemistry and Materials Science, University of Szeged, H-6720 Rerrich Béla tér 1, Szeged, Hungary

^hLaboratory of Nonlinear Chemical Dynamics, Institute of Chemistry, Eötvös Loránd University, H-1117, Pázmány Péter stny. 1/A, Budapest, Hungary;

ⁱHU-REN–BME Condensed Matter Physics Research Group, Budapest University of Technology and Economics, H-1111 Budafoki út 8, Budapest, Hungary

1. SEM, PXRD, BET, and BJH measurements

The formed crystals were investigated via scanning electron microscopy (SEM, Hitachi S-4700) by applying a secondary electron detector (Everhart–Thornley detector) and 20 kV accelerating voltage. The dry residue was placed onto conducting tape and gold sputtering was performed to maintain appropriate electrical conductance.

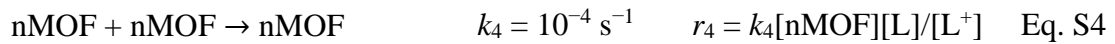
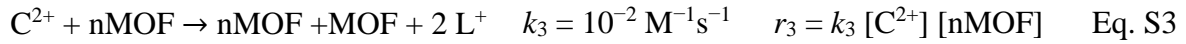
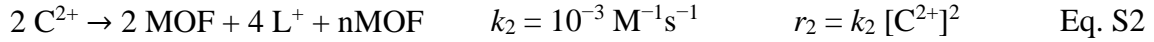
The powder X-ray diffraction measurements (PXRD) were applied to determine the crystalline phase of ZIF-8 crystals. The dry precipitate sample was placed on a monocrystalline silicon ingot and investigated with an X-ray diffractometer (Rigaku MiniFlex II Desktop X-ray Diffractometer) with $\text{CuK}\alpha$ ($\lambda = 0.1542$ nm) as a radiation source (30 kV accelerating voltage, 15 mA current) at ambient temperature in the $2\Theta = 5 - 50^\circ$ range applying 0.02° step size and $2^\circ/\text{min}$ scan rate.

The nitrogen adsorption data was evaluated via Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods which provided us with the specific surface area and pore size distribution, respectively. Before the nitrogen adsorption measurements, samples were degassed for 2 days at 180°C . Nitrogen adsorption data were collected with a Nova 3000 (Quantachrome, USA) instrument. The range of 0.05-0.35 relative pressure was used to determine the specific surface area, and the desorption band of the isotherm was applied for the BJH method.

2. Numerical model

2.1. Kinetic model

In the simulations, we used the following kinetic model:



L, M²⁺, C²⁺, MOF, nMOF, and L⁺ are the organic linker, zinc cation, intermediate complex, zinc ions in the formed zeolitic imidazolate framework-8, crystal of the zeolitic imidazolate framework-8, and the deprotonated form of the organic linker, respectively. The reaction rate constants in the kinetic model were arbitrarily selected. The relative size was calculated as [MOF]/[nMOF]. Eq. S1 describes the formation of a positively charged intermediate complex, which can further nucleate (Eq. S2). Eqs S3 and S4 present the crystal growth by reacting with the intermediate species and aggregation of crystals, respectively. Eq. S5 describes the protonation and deprotonation of the linker (2-MIM). The reaction rate of reaction Eq. S4 is inversely proportional to the relative charge.

2.2. Numerical simulations

The reaction–diffusion–ionic migration equations, mathematically second-order partial differential equations (Eq. 1 in the text), were solved numerically using the method of lines technique: spatial discretization of the partial differential equations on an equidistant 1D grid with the size of 5.0 cm combined with a forward Euler method for the integration in time. The total time of the simulations was 3×10⁵ s. The applied initial conditions in the computational domain (gel) can be found in Table S1. The concentration of the inner salt (potassium nitrate) in the model was calculated based on the conductivity measured in experiments ($EC = 70 \times 10^{-6}$ S) using relationship $EC = \frac{F^2}{RT \sum D_i z_i^2 c_i}$ ($D = 10^{-9}$ m²/s for charged chemical species in the system, where D is the diffusion coefficient). Solving diffusion term, we applied $D = 10^{-9}$ m²/s for all chemical species except MOF and nMOF, they cannot diffuse and be affected by

an electric field. Dirichlet boundary conditions (fixed concentrations at the boundaries) were applied for all chemical species in the model ($c_i(x = 0, t) = c_{ia}$, $c_i(x = L, t) = c_{ic}$), where c_{ia} , c_{ic} , and L are concentrations of the chemical species at the anodic and cathodic sites (for values see Table S1), and the length of the computational domain (gel column), respectively. We used 1.67×10^{-2} cm and 1.5 s for the grid spacing and time step, respectively.

Table S1. Initial concentrations of the chemical species used in the simulations.

Chemical species	Concentrations at the anodic side (mM)	Concentrations at the cathodic site and gel (mM)
MOF	0	0
Zn ²⁺	30	0
Ac ⁻	60	0
L	0	300
C ²⁺	0	0
K ⁺	9.32	9.32
NO ₃ ⁻	9.32	9.32
OH ⁻	2×10^{-4}	1.00
L ⁺	0	0

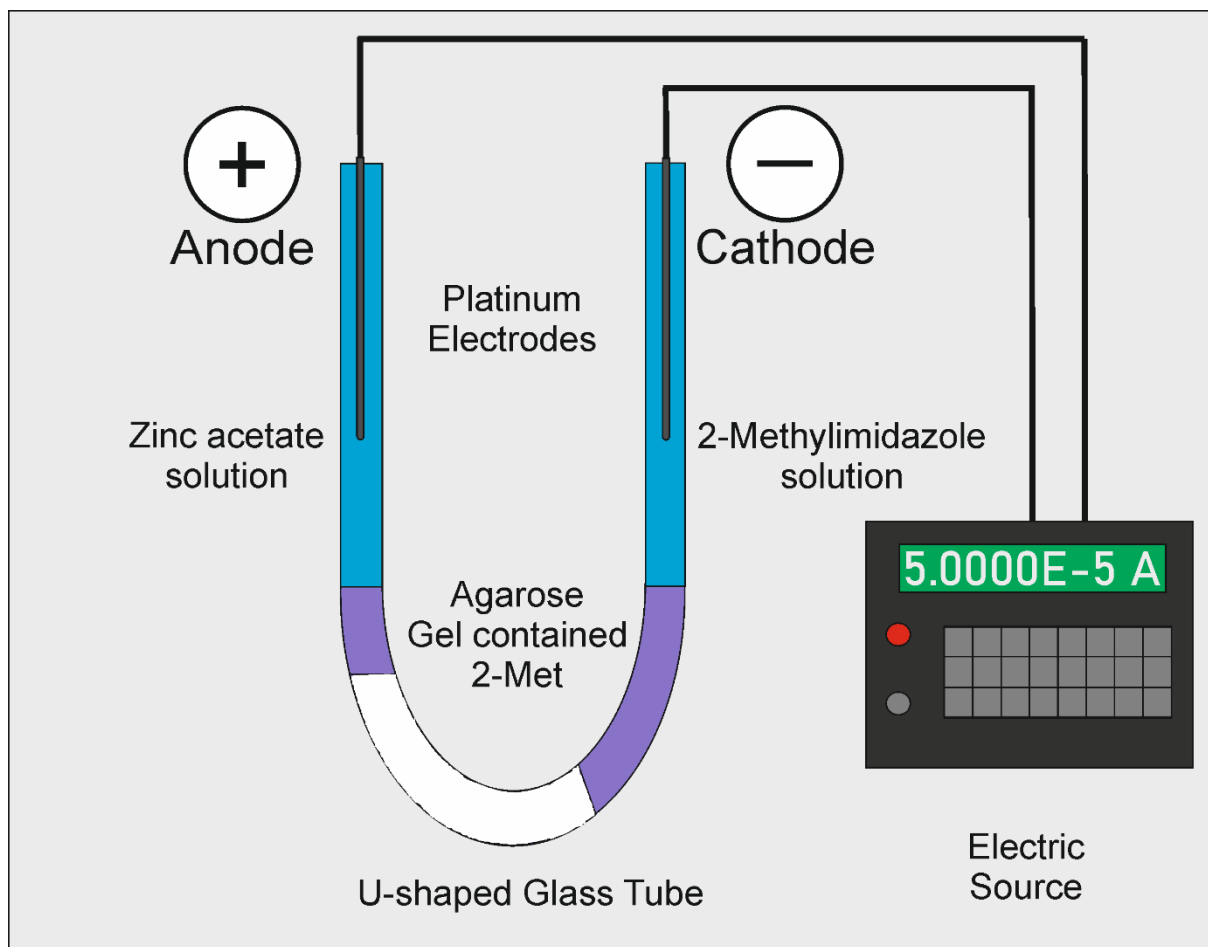


Fig. S1 Experimental setup of the investigation of the ZIF-8 formation in a gel using a direct electric field.

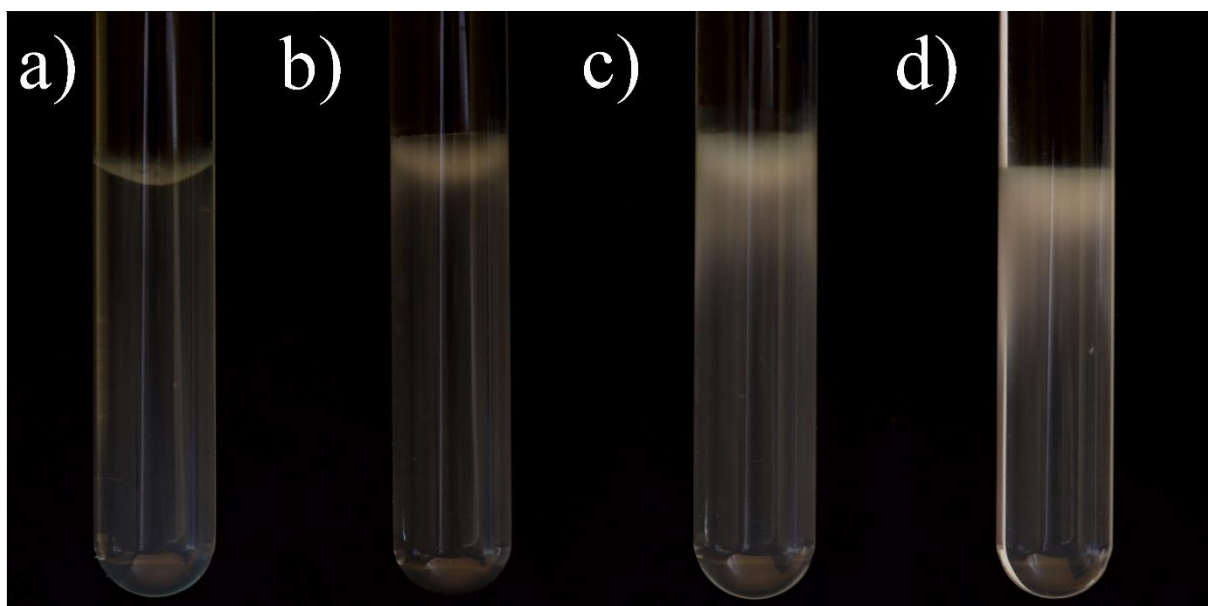


Fig. S2 Formation of ZIF-8 in the gel matrix (1% w/v of agarose; H₂O/DMF volumetric ratio was 1:1) in test tubes after 3 days of reaction and diffusion of ZIF precursors at room temperature. The zinc cations (zinc acetate) were homogeneously distributed in the agarose gel. The solution of 2-MIM was placed on top of the solid gel; (a) [Zn²⁺] = 5.0 mM and [2-MIM] = 50 mM, (b) [Zn²⁺] = 10.0 mM and [2-MIM] = 100 mM, (c) [Zn²⁺] = 20.0 mM and [2-MIM] = 200 mM, and (d) [Zn²⁺] = 30.0 mM and [2-MIM] = 300 mM. The diameter of the test tubes was 1.0 cm.

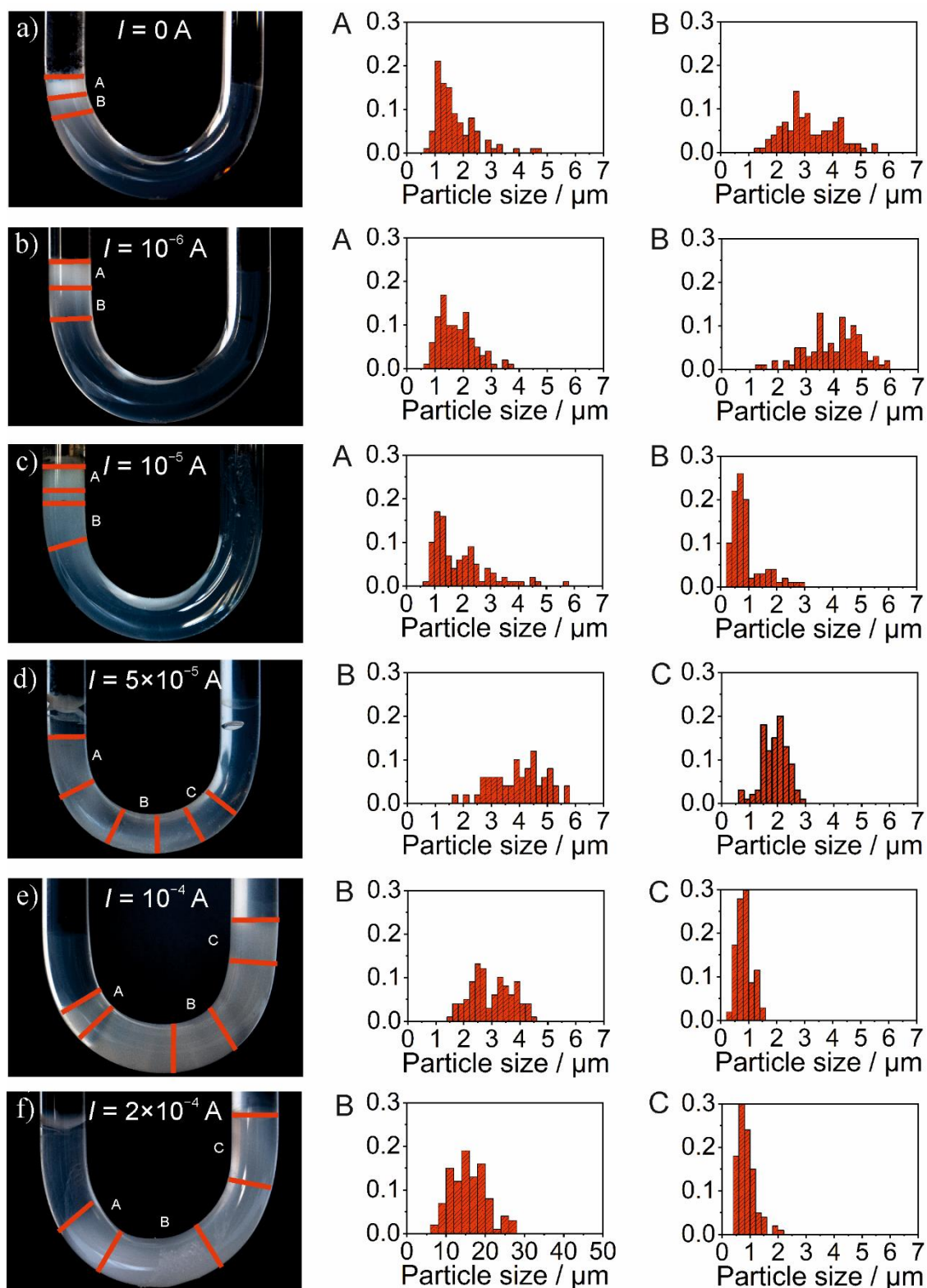


Fig. S3 Effect of an electric field on the distribution of the precipitate in the tube (optical photographs) and particle size distribution (using SEM micrographs) extracted from different segments of the agarose gel: a) diffusion ($I = 0$), b) $I = 1 \mu\text{A}$; c) $I = 10 \mu\text{A}$; d) $I = 50 \mu\text{A}$; e) $I = 100 \mu\text{A}$; and f) $I = 200 \mu\text{A}$. A, B, and C denote the segments of the agarose gel from which the particles were extracted after 3 days.

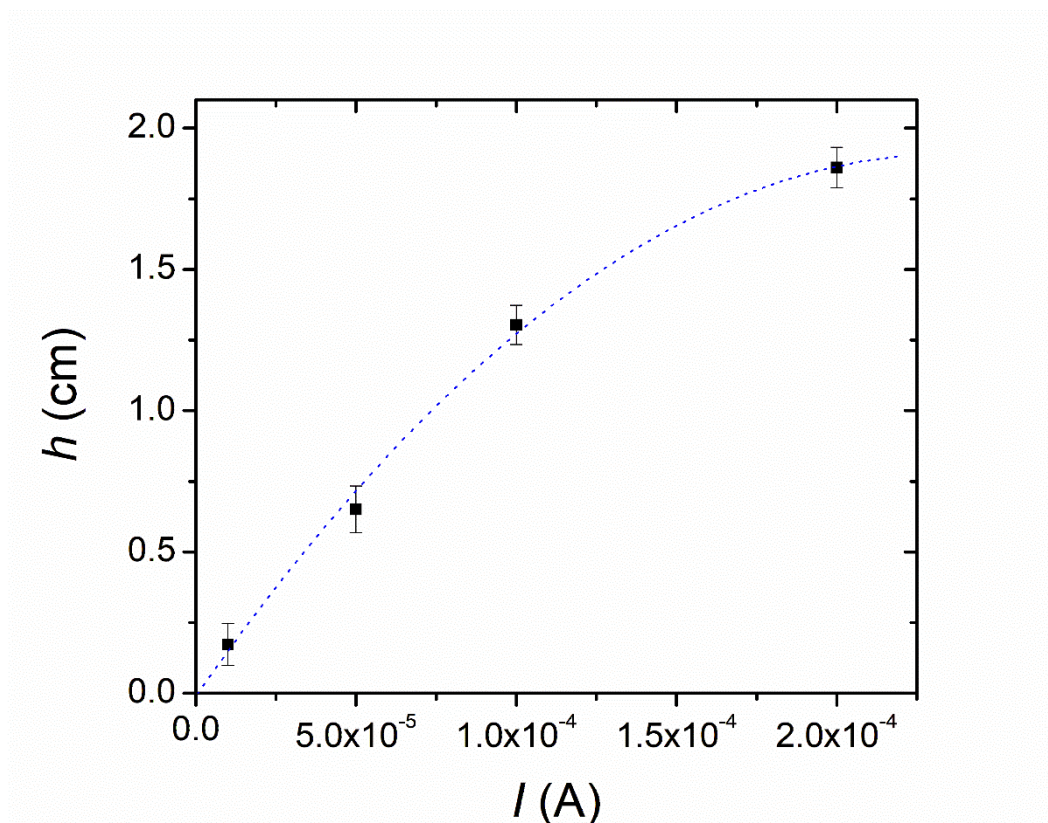


Fig. S4 Effect of the electric current (I) on the length of the precipitation-free zone (h) in the gel at the anodic side. The dotted line is only to guide the eye.

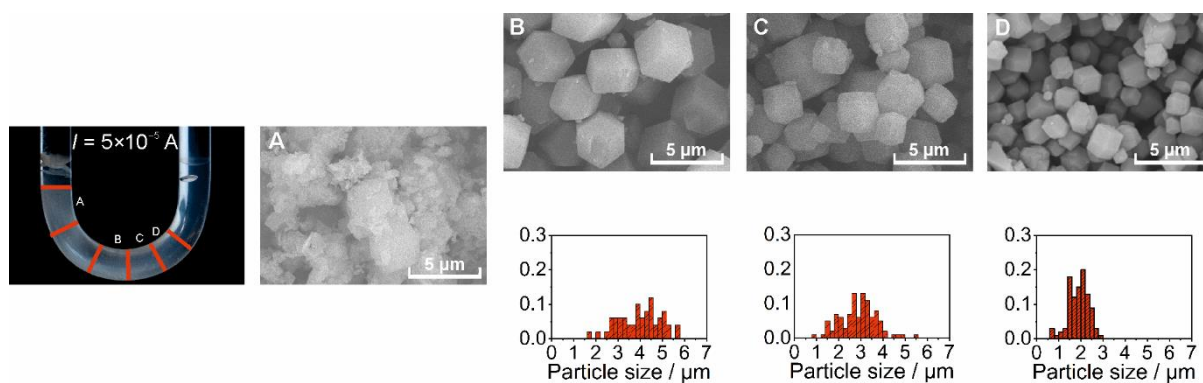


Fig. S5 Effect of an electric field on the distribution of the precipitate in the tube (optical photograph), morphology of the ZIF-8 particles, and particle size distribution (using SEM micrographs) extracted from different segments of the agarose gel using $I = 50 \mu\text{A}$. A, B, C, and D denote the segments of the agarose gel from which the particles were extracted after 3 days.

Table S2. Statistical analysis of the ZIF-8 samples: average particle size and standard deviation of the particles extracted from the different segments of the gel medium. (See the optical photographs of the U-shaped glass tubes in **Fig. 1**).

<i>Current / mA</i>	<i>Average voltage / V</i>	<i>Part of the gel</i>	<i>Average Particle size / μm</i>	<i>Standard deviation / μm</i>	<i>Particles measured</i>
Control (only diffusion, $I = 0$ mA)		A	1.71	± 0.74	100
		B	3.19	± 0.93	100
0.001	1.56	A	1.77	± 0.63	101
		B	3.98	± 0.97	100
0.01	4.54	A	1.90	± 0.99	100
		B	0.90	± 0.56	100
0.05	14.55	B	3.98	± 0.94	50
		C	2.89	± 0.81	100
		D	1.90	± 0.45	100
0.1	35.16	B	3.03	± 0.90	100
		C	0.85	± 0.27	104
0.2	92.00	B	15.73	± 4.59	100
		C	0.87	± 0.31	100

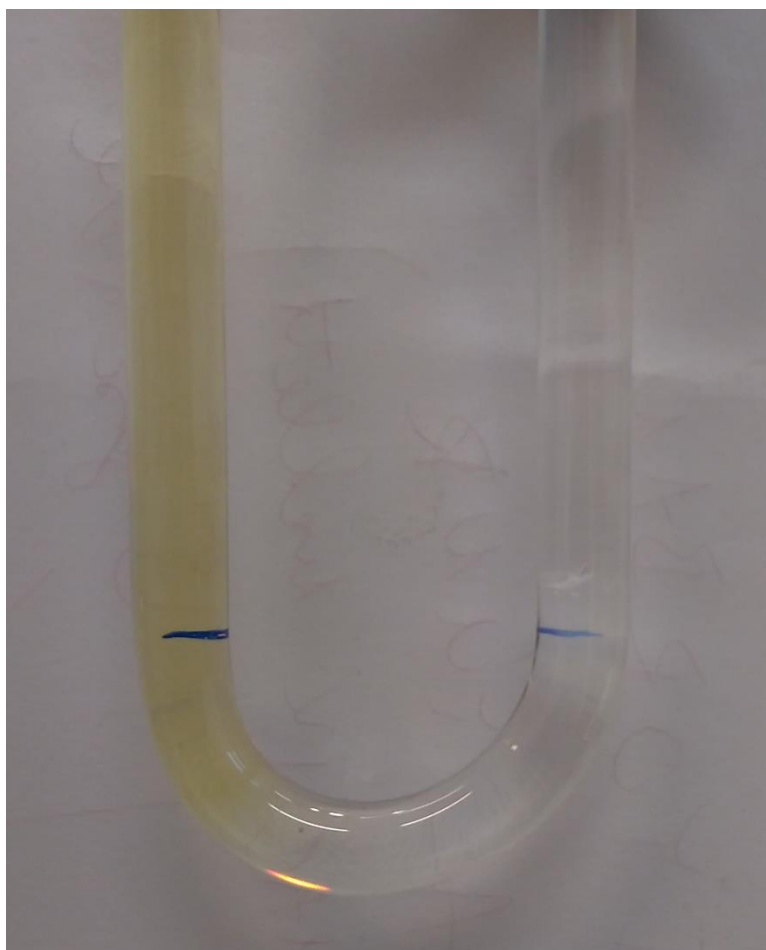


Fig. S6 Oxidation of 2-MIM by an electric field at the anodic site. The yellow color corresponds to the oxidized form of 2-MIM.¹ Blue lines indicate the liquid–gel interface.

References

1 M. Itatani, N. Német, N. Valletti, G. Schuszter, P. Prete, P. Lo Nostro, R. Cucciniello, F. Rossi and I. Lagzi, *ACS Sustainable Chem. Eng.*, 2023, **11**, 13043–13049.