Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Application of a chemical clock in material design: chemically programmed synthesis of zeolitic imidazole framework-8

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1. Experimental

1.1 Sample preparation

Formaldehyde solution (HCOH, Sigma-Aldrich), sodium sulfite (Na_2SO_3 Sigma Aldrich), sodium metabisulfite ($Na_2S_2O_5$, Sigma Aldrich), 2-methylimidazole ($CH_2C_3H_2N_2H$, Sigma-Aldrich), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, Sigma-Aldrich), and D-(+)-glucono-δ-lactone ($C_6H_{10}O_6$, Sigma-Aldrich) were used without further purification. The aqueous solutions of all chemicals (except formaldehyde solution) were always prepared daily freshly before the measurements.

Kinetic experiments with the turbidity measurements were carried out in a round glass cuvette having an optical path length (diameter) and volume of 2.8 cm and 24 mL, respectively. The pH was monitored by a glass microelectrode (Mettler Toledo) and the turbidity was monitored by a UV−Vis spectrophotometer (VWR UV−1600PC) in kinetic mode ($\lambda = 600$ nm) connected to PC. The solutions of the reactants were consecutively added to the cell as follows: sulfite−metabisulfite solution, 2-methylimidazole solution, zinc sulfate solution, and finally formaldehyde solution (in one set of experiments it contained glucono-δ-lactone as well). The initial pH of the reaction mixture was pH ~ 5.5, and it was stirred by using a magnetic stirrer at 300 rpm.

After 24 hours, the formed white precipitate was filtered by using a 0.45 μm syringe filter (cellulose-acetate) and washed once with 5 mL distilled water and twice with 3 mL DMF (*N*,*N*-dimethylformamide). Then the filter was dried under ambient conditions at 20 ± 0.5 °C (~24 h), and the white precipitate was removed from the surface of the filter.

1.2 Characterization

The microstructures of the ZIF-8 samples were investigated via scanning electron microscopy (SEM, Hitachi S-4700 microscope) applying a secondary electron detector and 20 kV accelerating voltage. The dry precipitate was placed onto conducting tape and gold sputtering was performed to maintain appropriate electrical conductance.

Powder X-ray diffraction (PXRD) was applied to determine the crystalline phase of the samples. Dry precipitate samples were placed on a monocrystalline silicon ingot and investigated with an X-ray diffractometer (Rigaku MiniFlex II Desktop X-ray Diffractometer) with CuKα (= 0.1542 nm) as a radiation source (30 kV accelerating voltage, 15 mA current) at ambient temperature in the $2\Theta = 5 - 40$ ° range applying 0.02 ° step size.

2. The formation of ZIF-8 in the aqueous phase

The formation of ZIF-8 in the aqueous phase can be described by the following mechanism:

$$\mathrm{MIMH} \rightleftharpoons \mathrm{H^{+}} + \mathrm{MIM^{-}} \tag{1}$$

$$\mathrm{MIMH_2^{+}} \rightleftharpoons \mathrm{MIMH} + \mathrm{H^{+}} \tag{2}$$

$$\mathrm{Zn^{2+}} + 4\ \mathrm{MIMH} \rightleftharpoons \mathrm{Zn(MIMH)_4^{2+}} \tag{3}$$

$$\mathrm{Zn(MIMH)_4^{2+}} \rightleftharpoons \mathrm{H^{+}} + \mathrm{Zn((MIMH)_3\text{-}(MIM)^{+})} \tag{4}$$

$$\mathrm{Zn((MIMH)_3\text{-}(MIM))^{+}} \rightleftharpoons \mathrm{H^{+}} + \mathrm{Zn((MIMH)_2\text{-}(MIM)_2)} \tag{5}$$

$$\mathrm{Zn((MIMH)_2\text{-}(MIM)_2)} \rightleftharpoons \text{ZIF-8} + 2\ \mathrm{MIMH}. \tag{6}$$

Eqn 1 and 2 describe the deprotonation of 2-Met (pKa = 15.1) and protonated 2-Met (pKa = 7.85), respectively[1]. Based on the pKa values, in the aqueous phase two dominant forms of 2-Met exist, MIMH and $\mathrm{MIMH_2^{+}}$. The amount of $\mathrm{MIM^{-}}$ is negligible even at elevated pH (at pH ~ 11 the amount of $\mathrm{Met^{-}}$ is ~ 0.1 – 0.01% of the total amount of MIMH in the system (Fig. S5b). Therefore, the zinc cations coordinate with the neutral MIMH forming a charged complex ($\mathrm{Zn(MIMH)_4^{2+}}$, eqn (3)). The next stage of the formation of ZIF-8 is the deprotonation of the $\mathrm{Zn(MIMH)_4^{2+}}$ generating $\mathrm{Zn((MIMH)_2\text{-}(MIM)_2)}$ (eqn (4) and (5)). This process is feasible in a moderate alkaline environment since the reaction has pKa = 10.3[2]. The final step is the oligomerization of the units $\mathrm{Zn((MIMH)_2\text{-}(MIM)_2)}$ to ZIF-8 crystal (eqn (6)).

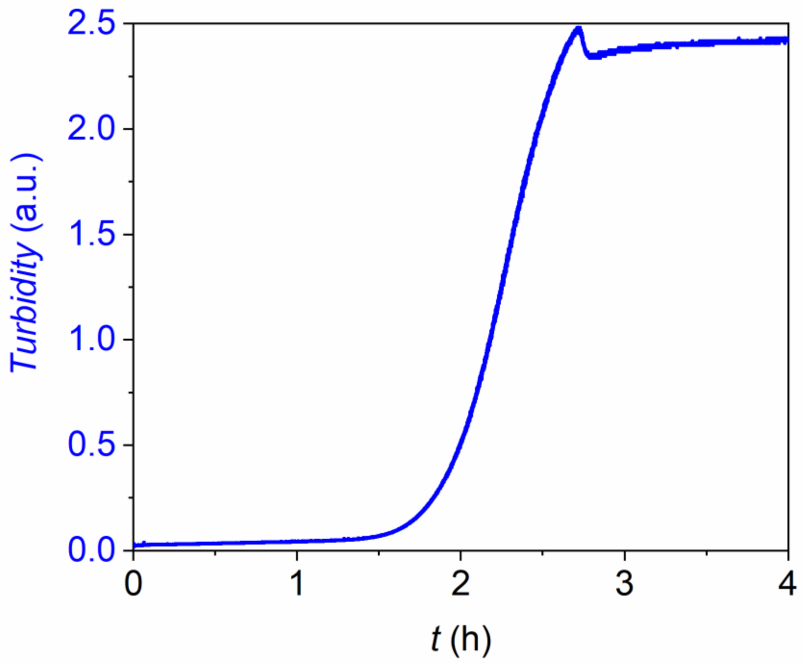

Figure S1 Turbidity change in the reaction of Zn^{2+} with 2-methylimidazole ($[Zn^{2+}]_0$ = 2 mM) and $[2\text{-Met}]_0$ = 100 mM).

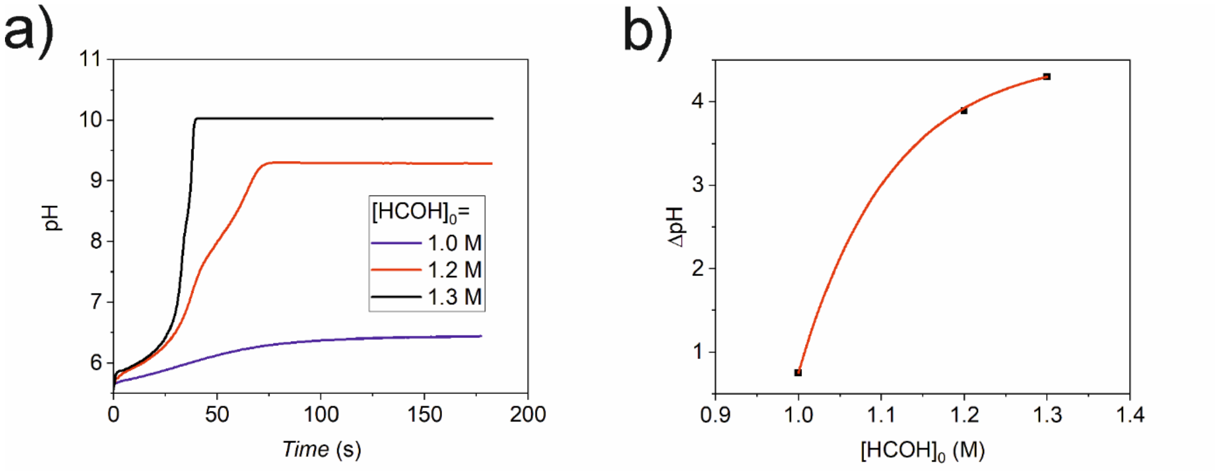

Figure S2 Effect of the initial concentration of the formaldehyde on the course of the pH (a) and pH change (b) in the methylene glycol–sulfite reactions ($[SO_3^{2-}]_0$ = 20 mM, $[HSO_3^-]_0$ = 1200 mM, $[Zn^{2+}]_0$ = 2 mM, and [2-Met]$_0$ = 100 mM). In (b) the solid line is the guide to the eyes.

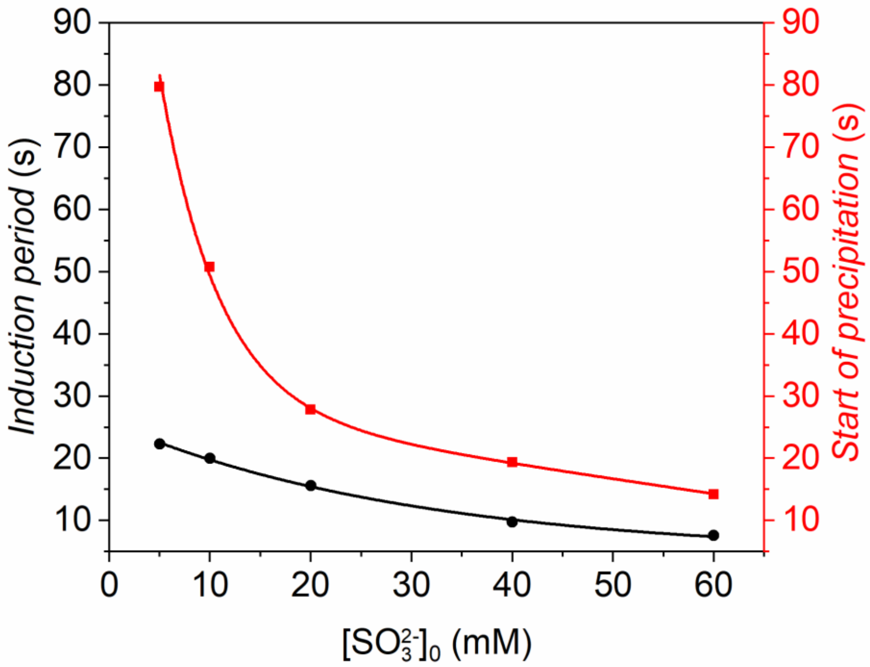

Figure S3 Dependence of the induction period (clock time) of the methylene glycol–sulfite clock reaction coupled to the Zn^{2+} – 2-methylimidazole reaction (black) and time of the start of the precipitation (red, defined as when the turbidity was greater than 0.001) on the initial sulfite concentration ([HSO$_3^-$]$_0$ = 1200 mM, [HCOH]$_0$ = 1200 mM, [Zn^{2+}]$_0$ = 2 mM, and [2-Met]$_0$ = 100 mM). The solid line is the guide to the eyes.

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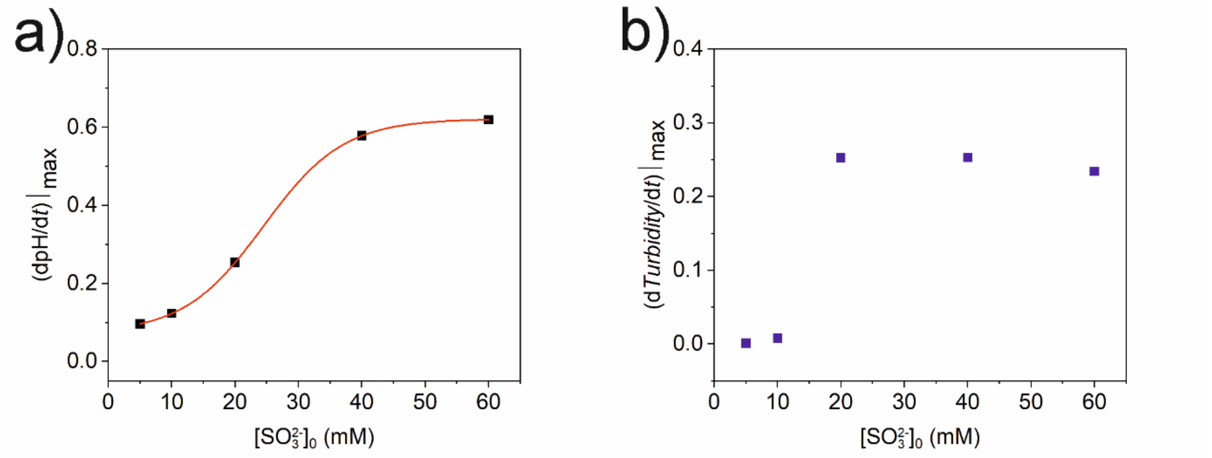

Figure S4 Dependence of the maximum rate of the pH (a) and turbidity (b) change on the sulfite concentration in the methylene glycol–sulfite clock reaction coupled to the Zn^{2+} – 2-methylimidazole reaction ($[HSO_3^-]_0$ = 1200 mM, $[HCOH]_0$ = 1200 mM, $[Zn^{2+}]_0$ = 2 mM, and $[2\text{-Met}]_0$ = 100 mM). The solid line is the guide to the eyes.

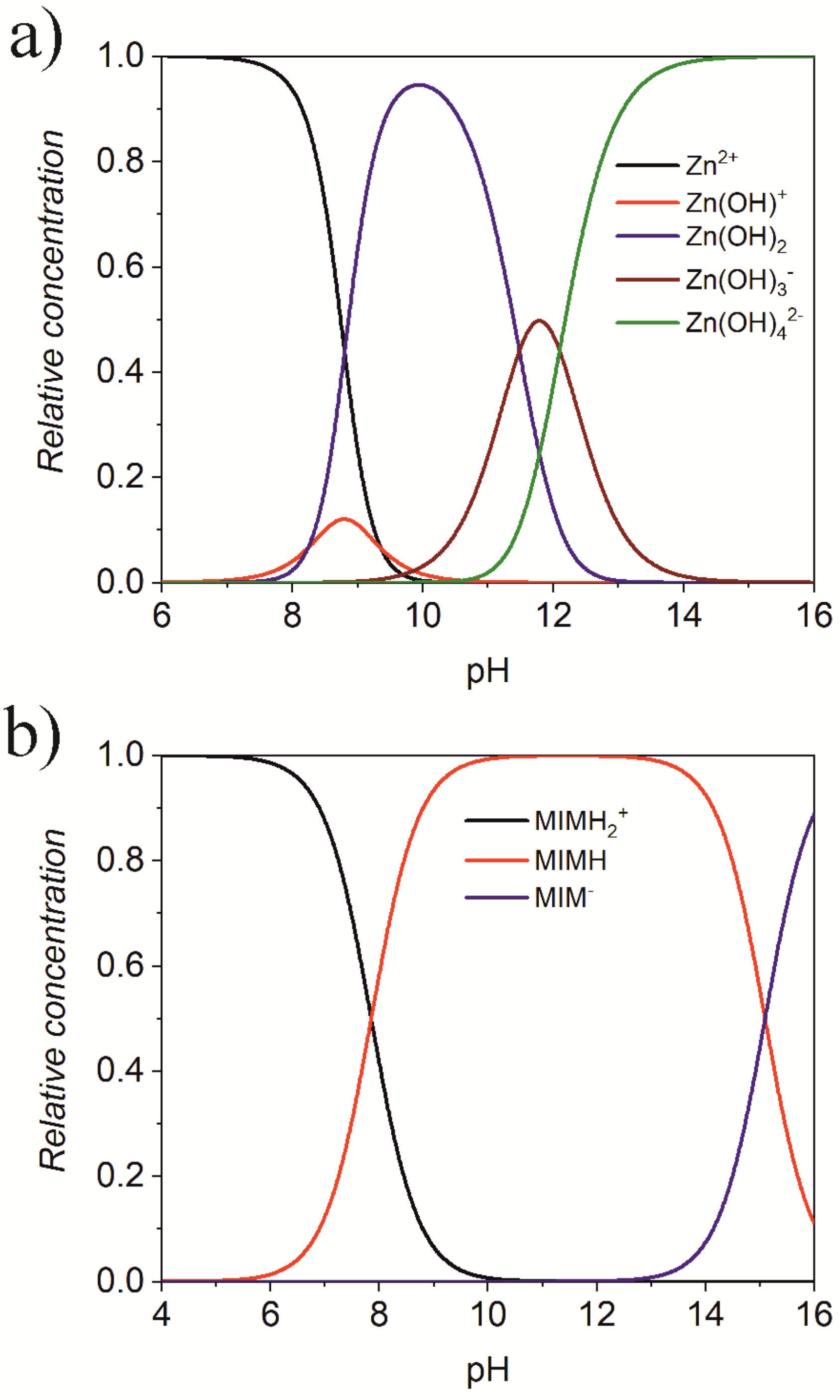

Figure S5 pH-dependent speciation of 2-methylimidazole (a) and zinc ion (b) in aqueous solution. The reaction rate coefficients were obtained from Ref 1.

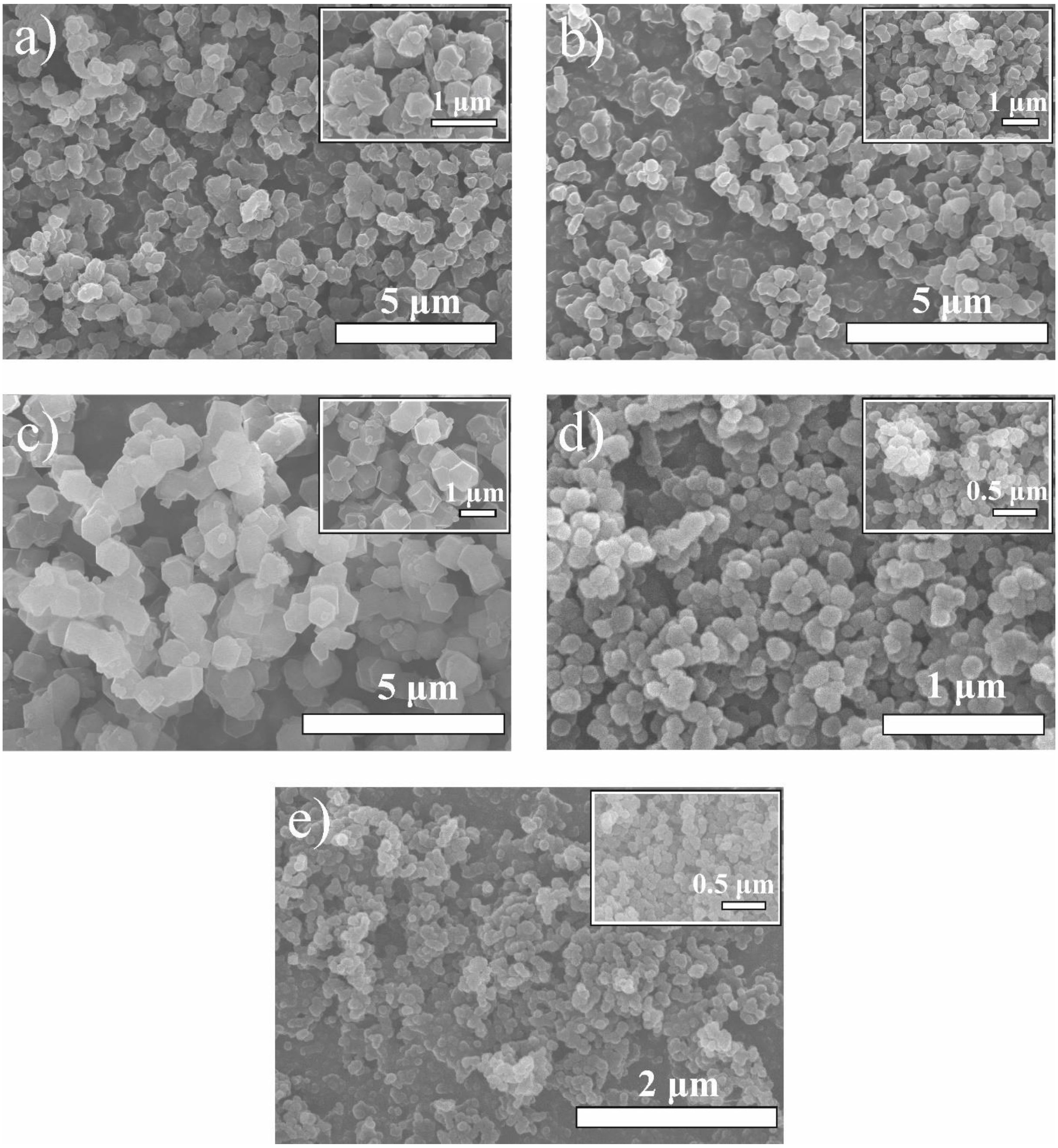

Figure S6 SEM micrographs of ZIF-8 particles synthetized using methylene glycol−sulfite reaction with different initial sulfite concentrations: (a) $[SO_3^{2-}]_0 = 5$ mM; (b) $[SO_3^{2-}]_0 = 10$ mM; (c) $[SO_3^{2-}]_0 = 20$ mM; (d) $[SO_3^{2-}]_0 = 40$ mM, and (e) $[SO_3^{2-}]_0 = 60$ mM ($[\text{formaldehyde}]_0 = 1200$ mM, $[HSO_3^{-}]_0 = 1200$ mM, $[Zn^{2+}]_0 = 2$ mM, and $[\text{2-Met}]_0 = 100$ mM). The samples were collected after 24 hours of the experiments.

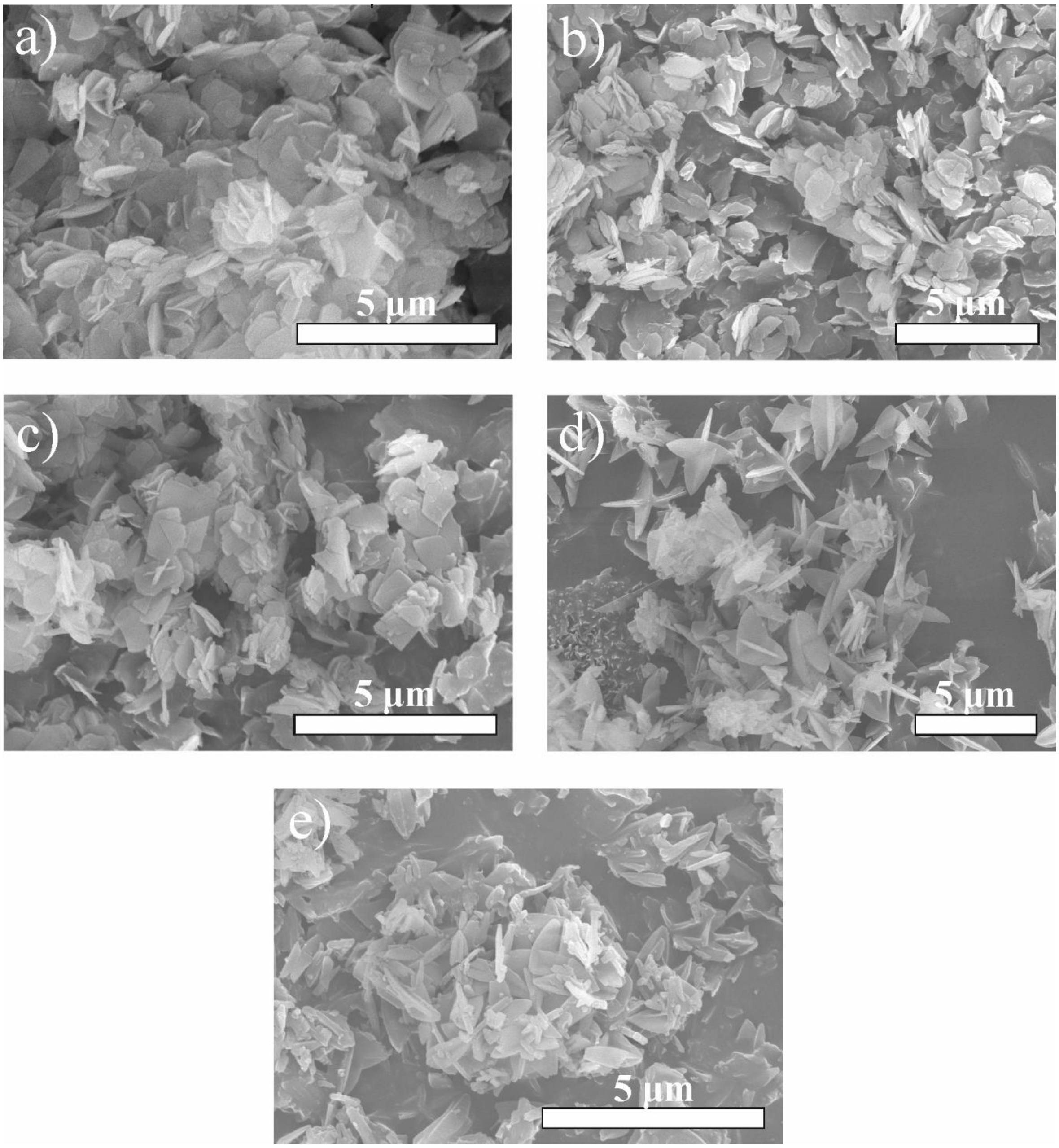

Figure S7 SEM micrographs of crystals synthetized in an aqueous phase using Zn^{2+} and 2-Met ($[Zn^{2+}]_0$ = 2 mM and $[\text{2-Met}]_0$ = 100 mM, in the absence of the methylene glycol–sulfite reaction) in a presence of an inert salt (KNO_3) to emulate the ionic strength of the clock reaction: (a) $[KNO_3]$ = 0, (b) $[KNO_3]$ = 2 mM, (c) $[KNO_3]$ = 92 mM M, (d) $[KNO_3]$ = 992 mM, and (e) $[KNO_3]$ = 2492 mM. The samples were collected after 24 hours of the experiments.

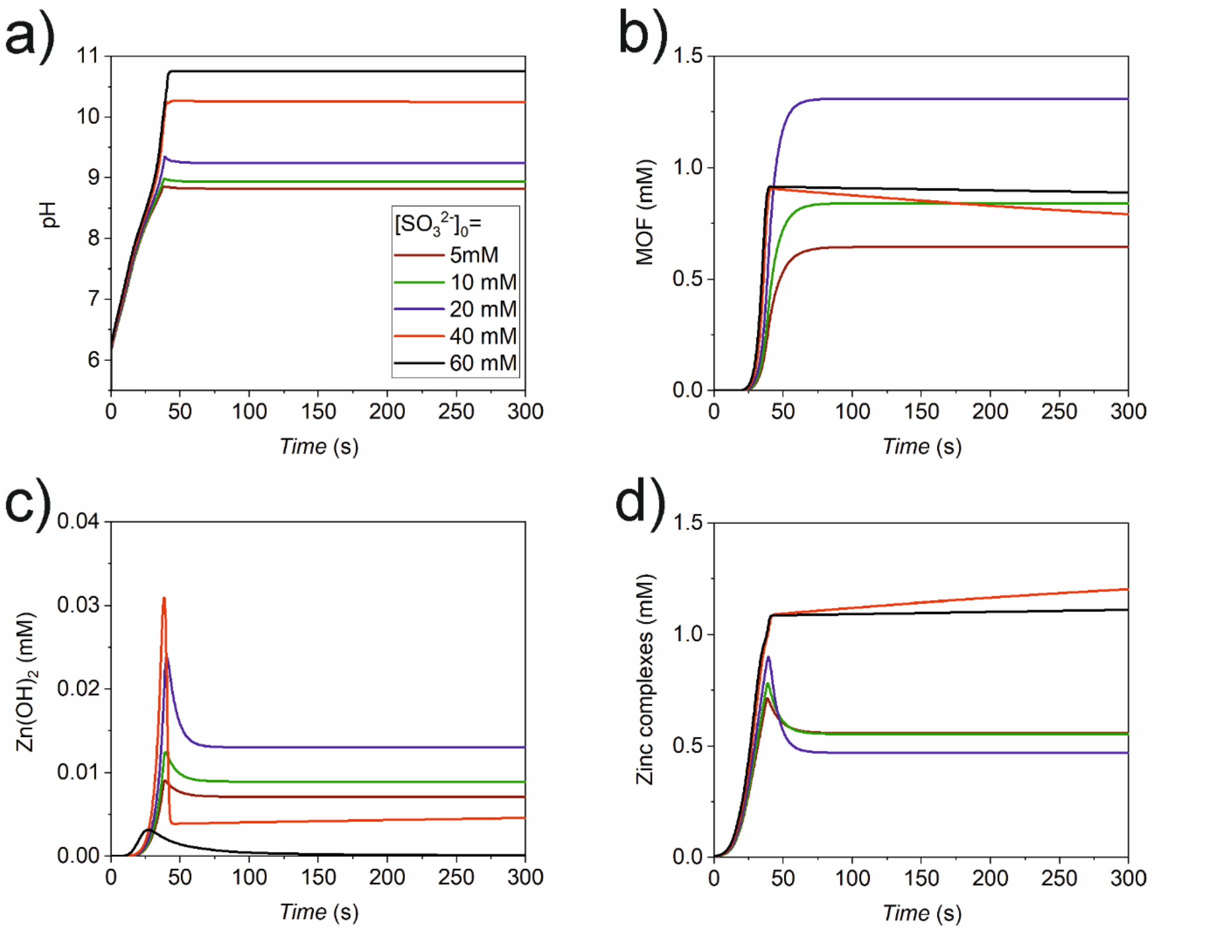

Figure S8 Time-resolved pH curves (a) and temporal changes of the concentrations of ZIF-8 (b), zinc hydroxide (c) and zinc complexes (d) in the methylene glycol–sulfite reactions in the presence of zinc ions ([Zn^{2+}]$_0$ = 2 mM) and 2-Methylimidazole ([2-Met]$_0$ = 100 mM) using various initial sulfite concentrations (5, 10, 20 40, and 60 mM) in numerical simulations.

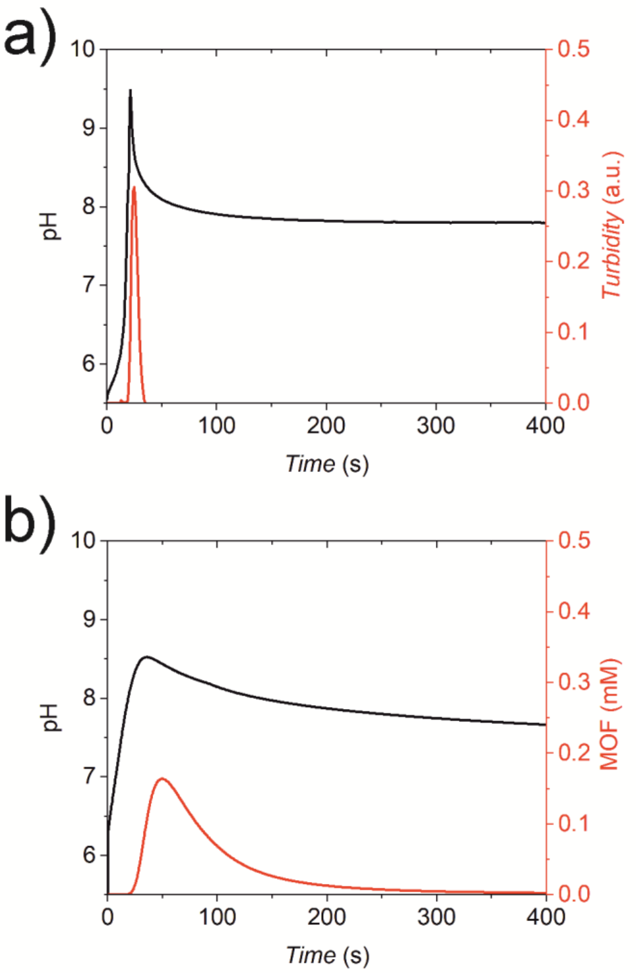

Figure S9 Time-resolved pH and turbidity (defined as absorbance at $\lambda = 600$ nm) curves of the methylene glycol–sulfite–glucono-δ-lactone reactions in an experiment (a) and time-resolved pH and concentration of ZIF-8 curves of the methylene glycol–sulfite–glucono-δ-lactone reactions in a numerical simulation (b) ($[\text{formaldehyde}]_0 = 1300$ mM, $[SO_3^{2-}]_0 = 60$ mM, $[HSO_3^-]_0 = 1200$ mM, $[\text{glucono-}\delta\text{-lactone}]_0 = 100$ mM), $[Zn^{2+}]_0 = 2$ mM), and 2-Met ($[\text{2-Met}]_0 = 100$ mM).

No.	Reaction	Rate law	Rate constants
R1	$\mathrm{CH_2(OH)_2 \rightleftharpoons CH_2O + H_2O}$	$(k_{b1} + k_{b1\mathrm{OH}}[\mathrm{OH^-}])[\mathrm{CH_2(OH)_2}]$ $- k_{1r}[\mathrm{CH_2O}]$	$k_{b1} = 5.50 \times 10^{-3}\ \mathrm{s^{-1}}$ $k_{b1\mathrm{OH}} = 2.10 \times 10^{3}\ \mathrm{M^{-1}s^{-1}}$ $k_{b1r} = 10\ \mathrm{s^{-1}}$
R2	$\mathrm{HSO_3^- \rightleftharpoons SO_3^{2-} + H^+}$	$k_{b2}[\mathrm{HSO_3^-}] - k_{b2r}[\mathrm{SO_3^{2-}}][\mathrm{H^+}]$	$k_{b2} = 3.10 \times 10^{3}\ \mathrm{s^{-1}}$ $k_{b2r} = 5 \times 10^{10}\ \mathrm{M^{-1}s^{-1}}$
R3	$\mathrm{CH_2O + SO_3^{2-} \rightarrow CH_2(O^-)SO_3^-}$	$k_{b3}[\mathrm{CH_2O}][\mathrm{SO_3^{2-}}]$	$k_{b3} = 5.40 \times 10^{6}\ \mathrm{M^{-1}s^{-1}}$
R4	$\mathrm{CH_2(O^-)SO_3^- + H^+ \rightleftharpoons CH_2(OH)SO_3^-}$	$k_{b4}[\mathrm{CH_2(O^-)SO_3^-}][\mathrm{H^+}]$ $- k_{b4r}[\mathrm{CH_2(OH)SO_3^-}]$	$k_{b4} = 1 \times 10^{10}\ \mathrm{M^{-1}s^{-1}}$ $k_{b4r} = 2 \times 10^{-3}\ \mathrm{s^{-1}}$
R5	$\mathrm{H_2O \rightleftharpoons H^+ + OH^-}$	$k_{b5} - k_{b5r}[\mathrm{OH^-}][\mathrm{H^+}]$	$k_{b5} = 1 \times 10^{-3}\ \mathrm{M^{-1}\,s^{-1}}$ $k_{b5r} = 1 \times 10^{11}\ \mathrm{Ms^{-1}}$
R6	$\mathrm{CH_2O + HSO_3^- \rightarrow CH_2(OH)SO_3^-}$	$k_{b6}[\mathrm{CH_2O}][\mathrm{HSO_3^-}]$	$k_{b6} = 4.50 \times 10^{2}\ \mathrm{M^{-1}s^{-1}}$
R7	$\mathrm{CH_2(OH)_2 + SO_3^{2-} \rightarrow CH_2(O^-)SO_3^- + H_2O}$	$k_{b7}[\mathrm{CH_2(OH)_2}][\mathrm{SO_3^{2-}}]$	$k_{b7} = 1.20\ \mathrm{M^{-1}s^{-1}}$
R8	$\mathrm{CH_2(OH)_2 + HSO_3^- \rightarrow CH_2(OH)SO_3^- + H_2O}$	$k_{b8}[\mathrm{CH_2(OH)_2}][\mathrm{HSO_3^-}]$	$k_{b8} = 1 \times 10^{-1}\ \mathrm{M^{-1}s^{-1}}$
R9	$\mathrm{GL \rightleftharpoons GA}$	$(k_{b9} + k_{b9\mathrm{OH}}[\mathrm{OH^-}])[\mathrm{GL}] - k_{b9r}[\mathrm{GA}]$	$k_{b9} = 1 \times 10^{-4}\ \mathrm{s^{-1}}$ $k_{b9\mathrm{OH}} = 4 \times 10^{3}\ \mathrm{M^{-1}s^{-1}}$ $k_{b9r} = 2 \times 10^{-5}\ \mathrm{s^{-1}}$
R10	$\mathrm{GA \rightleftharpoons GA^- + H^+}$	$k_{b10}[\mathrm{GA}] - k_{b10r}[\mathrm{GA^-}][\mathrm{H^+}]$	$k_{\mathrm{b10}} = 2.50 \times 10^{2}\ \mathrm{s^{-1}}$ $k_{b10r} = 1 \times 10^{6}\ \mathrm{M^{-1}s^{-1}}$
R11	$\mathrm{MIMH_2{}^+ \rightleftharpoons MIMH + H^+}$	$k_{m1}[\mathrm{MIMH_2{}^+}] - k_{m1r}[\mathrm{MIMH}][\mathrm{H^+}]$	$k_{\mathrm{m1}} = 1.41 \times 10^{1}\ \mathrm{s^{-1}}$ $k_{\mathrm{m1}} = 1 \times 10^{9}\ \mathrm{M^{-1}s^{-1}}$
R12	$\mathrm{MIMH + OH^- \rightleftharpoons MIM^- + H_2O}$	$k_{m2}[\mathrm{MIMH}][\mathrm{OH^-}] - k_{m2r}[\mathrm{MIM^-}]$	$k_{\mathrm{m2}} = 1 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}}$ $k_{\mathrm{m2}} = 1.26 \times 10^{11}\ \mathrm{s^{-1}}$
R13	$\mathrm{4\,MIMH + Zn^{2+} \rightleftharpoons Zn(MIMH)_4^{2+}}$	$k_{m3}[\mathrm{MIMH}]^4[\mathrm{Zn^{2+}}]$ $- k_{m3r}[\mathrm{Zn(MIMH)_4^{2+}}]$	$k_{\mathrm{m3}} = 1 \times 10^{4}\ \mathrm{M^{-3}\,s^{-1}}$ $k_{\mathrm{m3r}} = 1 \times 10^{1}\ \mathrm{s^{-1}}$
R14	$\mathrm{Zn((MIMH)_2 - (MIM)_2) \rightleftharpoons ZIF + 2\,MIMH}$	$k_{m4}[\mathrm{Zn((MIMH)_2 - (MIM)_2)}]$ $- k_{m4r}[\mathrm{ZIF}][\mathrm{MIMH}]^2$	$k_{\mathrm{m4}} = 1 \times 10^{3}\ \mathrm{s^{-1}}$, $k_{\mathrm{m4r}} = 1 \times 10^{1}\ \mathrm{M^{-2}\,s^{-1}}$
R15	$\mathrm{Zn(MIMH)_4^{2+} + OH^- \rightleftharpoons}$ $\mathrm{Zn\big((MIMH)_3 - (MIM)\big)^+ + H_2O}$	$k_{m5}[\mathrm{Zn(MIMH)_4^{2+}}][\mathrm{OH^-}]$ $- k_{m5r}[\mathrm{Zn\big((MIMH)_3 - (MIM)\big)^+}]$	$k_{\mathrm{m5}} = 1 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}}$ $k_{\mathrm{m5r}} = 2 \times 10^{5}\ \mathrm{s^{-1}}$
R16	$\mathrm{Zn\big((MIMH)_3 - (MIM)\big)^+ + OH^- \rightleftharpoons}$ $\mathrm{Zn((MIMH)_2 - (MIM)_2) + H_2O}$	$k_{m6}[\mathrm{Zn\big((MIMH)_3}$ $\mathrm{- (MIM)\big)^+}][\mathrm{OH^-}]$ $- k_{m6r}[\mathrm{Zn((MIMH)_2 - (MIM)_2)}]$	$k_{\mathrm{m6}} = 1 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}}$ $k_{\mathrm{m6r}} = 2 \times 10^{5}\ \mathrm{s^{-1}}$
R17	$\mathrm{Zn^{2+} + OH^- \rightleftharpoons Zn(OH)^+}$	$k_{z1}[\mathrm{Zn^{2+}}][\mathrm{OH^-}] - k_{z1r}[\mathrm{Zn(OH)^+}]$	$k_{\mathrm{z1}} = 1 \times 10^{9}\ \mathrm{M^{-1}s^{-1}}$ $k_{\mathrm{z1r}} = 9.09 \times 10^{3}\ \mathrm{s^{-1}}$
R18	$\mathrm{Zn(OH)^+ + OH^- \rightleftharpoons Zn(OH)_2}$	$k_{z2}[\mathrm{Zn(OH)^+}][\mathrm{OH^-}]$ $- k_{z2r}[\mathrm{Zn(OH)_2}]$	$k_{\mathrm{z2}} = 1 \times 10^{9}\ \mathrm{M^{-1}s^{-1}}$ $k_{\mathrm{z2r}} = 5 \times 10^{5}\ \mathrm{s^{-1}}$
R19	$\mathrm{Zn(OH)_2 + OH^- \rightleftharpoons Zn(OH)_3^-}$	$k_{z3}[\mathrm{Zn(OH)_2}][\mathrm{OH^-}]$ $- k_{z3r}[\mathrm{Zn(OH)_3^-}]$	$k_{\mathrm{z3}} = 1 \times 10^{9}\ \mathrm{M^{-1}s^{-1}}$ $k_{\mathrm{z3r}} = 3.23 \times 10^{3}\ \mathrm{s^{-1}}$
R20	$\mathrm{Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}}$	$k_{z4}[\mathrm{Zn(OH)_3^-}][\mathrm{OH^-}]$ $- k_{z4r}[\mathrm{Zn(OH)_4^{2-}}]$	$k_{\mathrm{z4}} = 1 \times 10^{9}\ \mathrm{M^{-1}s^{-1}}$ $k_{\mathrm{z4r}} = 4.67 \times 10^{4}\ \mathrm{s^{-1}}$

Table S1 Chemical reactions, rate laws, and rate constants used in the numerical kinetic model of the methylene glycol-sulfite (gluconolactone) and $\mathrm{Zn^{2+}}$– 2-methylimidazole reactions, where GL is glucono-δ-lactone; GA is protonated and $\mathrm{GA^-}$ is deprotonated gluconic acid, MIMH is 2-methylimidazole, $\mathrm{MIMH_2{}^+}$ is double protonated and $\mathrm{MIM^-}$ is deprotonated 2-methylimidazole, and ZIF is ZIF-8. Data are taken from the literature (Refs [1] and [3]) except reaction rate coefficients in R13 and 14. These reaction rate coefficients were adjusted in this study.

Chemical species	Initial concentrations (*t* = 0) / M
$\mathrm{CH_2(OH)_2}$	1.2
$\mathrm{HSO_3^-}$	1.1280
$\mathrm{SO_3^{2-}}$	between 5×10^{-2} and 6×10^{-2}
GL	0 or 1×10^{-1}
$\mathrm{Zn^{2+}}$	2×10^{-3}
MIMH	1×10^{-1}
$\mathrm{CH_2O}$	0
$\mathrm{H^+}$	$5\times10^{-3}+0.5[\mathrm{SO_3^{2-}}]_0$
$\mathrm{CH_2(O^-)SO_3^-}$	0
$\mathrm{CH_2(OH)SO_3^-}$	0
$\mathrm{OH^-}$	10^{-9}
GA	0
$\mathrm{GA^-}$	0
$\mathrm{MIMH_2}^+$	0
$\mathrm{MIM^-}$	0
$\mathrm{Zn(MIMH)_4^{2+}}$	0
$\mathrm{Zn((MIMH)_2-(MIM)_2)}$	0
ZIF	0
$\mathrm{Zn\big((MIMH)_3-(MIM)\big)^+}$	0
$\mathrm{Zn(OH)^+}$	0
$\mathrm{Zn(OH)_2}$	0
$\mathrm{Zn(OH)_3^-}$	0
$\mathrm{Zn(OH)_4^{2-}}$	0

Table S2 The list of the chemical species and their initial concentrations in the methylene glycol–sulfite (gluconolactone) and $\mathrm{Zn^{2+}}$– 2-methylimidazole reactions used in the numerical model.

References:

1 K. Kida, M. Okita, K. Fujita, S. Tanaka and Y. Miyake, *CrystEngComm*, 2013, **15**, 1794.

2 M. Jian, B. Liu, R. Liu, J. Qu, H. Wang and X. Zhang, *RSC Adv*, 2015, **5**, 48433–48441.

3 K. Kovacs, R. McIlwaine, K. Gannon, A. F. Taylor, S. K. Scott, *J Phys Chem A*, 2005, **109**, 283–288.