Electronic Supplementary Information (ESI)

Surface acid-base catalytic activity of ZIF-8 revealed by super-resolution fluorescence microscopy

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Experimental details.

Materials and synthetic procedures:

Synthesis of ZIF-8 was based on the procedure described by Bux et al.[1] A solid mixture of 0.539 g zinc chloride (>98.5%, Acros Organics), 0.486 g 2- methylimidazole (>97%, TCI) and 0.270 sodium formate (>99.5%, Merck) was dissolved in 40 ml methanol (>99.8%, Honeywell) by ultra sonic treatment. Afterwards the solution was placed into a 100 ml Teflon autoclave and heated in a microwave oven (Microsynth, Milestone) with a rate of 8°C min^{-1} to 100°C and stayed at that temperature for 4 h. After cooling, the precipitated crystals were filtered and washed with methanol and dried for 1 day over silica gel at room temperature.

ZIF-8 modification was based on the procedure described by Wee et al.[2] 0.075 g of oleic acid (>97%, Acros organics), 2.5 g of tert-butanol (>99%, Sigma-Aldrich) and 0.033 g of ZIF-8 catalyst were added to a 20 ml stainless steel reactor and heated in oil bath with a rate of 8°C min^{-1} to 150°C and stayed at that temperature for 20 h. After cooling, modified ZIF-8 crystals were separated by centrifugation and washed with methanol and dried for 1 day over silica gel at room temperature.

To remove traces of oleic acid, modified ZIF-8 sample was washed with excess of 1-heptanol (>98%, Sigma-Aldrich), heptane(>99%, Acros organics), methanol solution of 2-methylimidazol, and methanol. Then, modified ZIF-8 crystals were separated by centrifugation and dried for 1 day over silica gel at room temperature. After that, the sample was tested for catalytic activity (Figure S2). Further, the sample was evacuated at 250°C and under 0.08 mBar vacuum, what caused sample to become brightly orange-coloured and unsuitable for further fluorescence microscopy investigation due to overwhelming background fluorescence.

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Fluorescein diacetate (FDA) (>99%, Sigma-Aldrich) was additionally purified by the means of preparative High-Performance Liquid Chromatography (HPLC). HPLC was conducted on Waters 996 with Waters 600-controller and polar column Alltech Prevail C18 (5 µm particle size, 15 cm length and 22 mm diameter). The separation started with 50:50 mixture of water and acetonitrile and then was gradually switched to pure acetonitrile.

MilliQ water for hydrolysis reaction was obtained from water purification system Synergy UV (Merck Millipore).

Fluorescence microscopy:

For the microscopy experiments, crystals were spin-casted on a clean cover glass (thickness #1). Liquid phase experiments were performed in 1 ml of water solution with a concentration of FDA of $5 \cdot 10^{-8}$ M added to polytetrafluoroethylene container sealed to the glass cover slip via a silicone rubber gasket.

The NASCA investigation was conducted on a wide-field fluorescence microscopy setup based on an inverted epi-fluorescence inverted microscope IX71 (Olympus) platform equipped with an oil immersion objective lens (100X, 1.4 NA, Olympus) and a Diode-Pumped Solid State Excelsior laser (Spectra-Physics). The latter provided a laser excitation with λ = 491 nm of 25 W/cm^2 power on the sample. Fluorescence imaging (505 nm long pass filter) was performed using an ImagEM Enhanced C9100-23B EM-CCD camera (Hamamatsu). Further single molecule identification, localization and generation of NASCA images were performed using an in-house developed set of open-source plugin routines (https://bitbucket.org/pdedecker/localizer)[3] for IgorPro v.6.34A software (Wavemetrics). The presented NASCA images were obtained by the accumulation of localized fluorescent emitters which appeared during reaction in the focal plane in the middle of the crystals for a recording duration indicated in the figure captions.

Spectrophotometric detection:

Bulk scale catalytic reaction was conducted in quartz cuvettes. 3 ml of water solution with a concentration of FDA of $5 \cdot 10^{-6}$ M was added to 0.5 mg of ZIF-8 catalyst and stirred at 25°C for 96 h. Fluorescein concentration was detected by the means of spectrophotometer Lambda 950 UV/Vis/NIR (PerkinElmer) using the optical adsorption at 491 nm wavelength.

Molecular geometry calculations:

Geometrical descriptors for FDA and oleic acid triglyceride were calculated using MarvinSketch.[4]

References:

1 H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. J. Caro, *J. Am. Chem. Soc.*, 2009, **131**, 16000–16001.

2 L. H. Wee, T. Lescouet, J. Ethiraj, F. Bonino, R. Vidruk, E. Garrier, D. Packet, S. Bordiga, D. Farrusseng, M. Herskowitz and J. A. Martens, *ChemCatChem*, 2013, **5**, 3562–3566.

3 P. Dedecker, S. Duwé, R. K. Neely and J. Zhang, *J. Biomed. Opt.*, 2012, **17**, 126008.

4 MarvinSketch with Calculator Plugins (version 15.9.21.0), calculation module developed by ChemAxon, http://www.chemaxon.com/products/marvin/marvinsketch/ , 2015

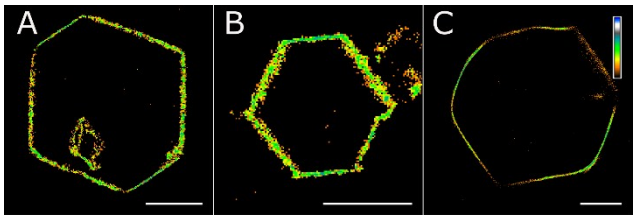

Figure S1. NASCA reactivity maps of FDA hydrolysis catalysed inside of several ZIF-8 crystals. Scale bars are 3 µm; maps are reconstructed for 50x50x800 nm^3 voxels (xyz) for the duration of ≈ 150 s; false colour shows the observed reaction rate in logarithmic scale from $2.2 \cdot 10^{-9}$ to $7.4 \cdot 10^{-7}$ $M \cdot s^{-1}$.

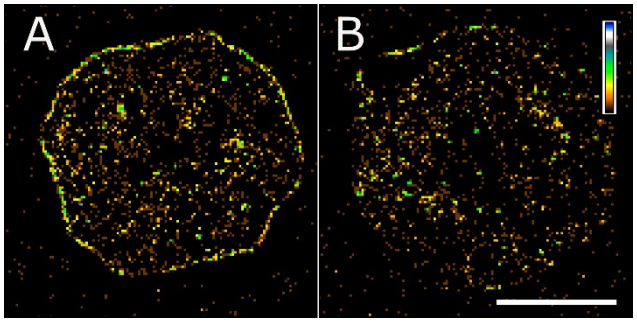

Figure S2. Effect of oleic acid removal attempt on activity of ZIF-8 crystals. NASCA reactivity maps of FDA hydrolysis catalysed inside of two exemplary etched ZIF-8 crystals. Scale bar is 5 µm, maps are reconstructed for 100x100x800 nm^3 voxels (xyz) for the duration of ≈ 500 s; false colour shows the observed reaction rate in logarithmic scale from $2.9 \cdot 10^{-10}$ to $3.0 \cdot 10^{-8}$ $M \cdot s^{-1}$.