Supporting Information for

Synthesis of the homochiral metal-organic framework DUT-129 based on a chiral dicarboxylate linker with 6 stereocenters

Christel Kutzscher, Daniel Janssen-Müller, Andreas Notzon, Ulrich Stoeck, Volodymyr Bon, Irena Senkovska, Stefan Kaskel* and Frank Glorius*

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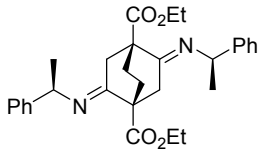
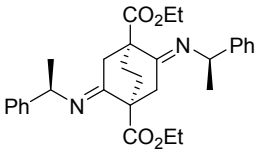
1. Linker Synthesis

1.1 Diethyl 2,5-bis(((*R*)-1-phenylethyl)imino)bicyclo[2.2.2]octane-1,4-dicarboxylate



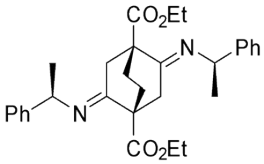
1



2

To racemic diethyl 2,5-dioxobicyclo-[2.2.2]octane-1,4-dicarboxylate (10 g, 35 mmol, 1.0 equiv.) and *p*-toluenesulfonic acid (330 mg,1.8 mmol, 0.05 equiv.) in dry toluene (50 mL) was added (*R*)-(+)-α-methylbenzylamine (9.94 mL, 77 mmol, 2.2 equiv.) and the mixture was heated at 110 °C with Dean-Stark apparatus. After 24 h, the mixture was cooled to rt and diluted with toluene (100 mL) and washed with sat. aq. $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$, concentrated under reduced pressure and preabsorbed on silica gel. Purification via silica gel column chromatography (pentane/EtOAc/Et_3N 92:7:1) gave the two diastereomeric products *S,S*-diastereoisomer **1** (6.8 g, 14 mmol, 40%) and *R,R*-diastereoisomer **2** (6.3 g, 13 mmol, 37%).

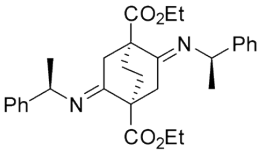
Diethyl (1*S*,2*E*,4*S*,5*E*)-2,5-bis(((*R*)-1-phenylethyl)imino)bicyclo[2.2.2]octane-1,4-dicarboxylate (1)



1

R_f (Pentan/EtOAc/NEt_3 92:7:1) = 0.35. **$[\alpha]_D^{20}$** = +49.8 (*c* = 1.00 in $CHCl_3$). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.52 – 7.02 (m, 10H, $CH_{arom.}$), 4.54 (q, 2H, *J* = 6.5 Hz, CH_2), 4.32 – 4.21 (m, 4H), 2.92 (dd, 2H, *J* = 18.0, 1.8 Hz, C*H*H), 2.63 (d, 2H, *J* = 17.9 Hz,CH*H*), 2.52 – 2.43 (m, 2H, C*H*H), 2.03 – 1.85 (m, 2H, CH*H*), 1.35 (d, 6H, *J* = 6.5 Hz, CH_3), 1.29 (t, 6H, *J* = 7.1 Hz, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 172.0 (COO), 166.5 (C=N), 145.2 ($C_{q,arom.}$), 128.2 ($C_{arom.}H$), 126.4 ($C_{arom.}H$), 126.3 ($C_{arom.}H$), 60.8, 58.4, 52.8, 34.5, 26.0, 24.7, 14.3. **MS-ES-EM (pos.)**: calculated for $[C_{30}H_{36}N_2O_4H]^+$: m/z = 489.2748, found: m/z = 489.2753, calculated for $[C_{30}H_{36}N_2O_4Na]^+$: m/z = 511.2567, found: m/z = 511.2574. **ATR-FTIR:** v/cm^{-1} = 2975 (s), 1732 (m), 1668 (m), 1449 (s), 1279 (s), 1248 (m), 1068 (m), 699 (m).

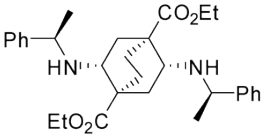
Diethyl (1*R*,2*E*,4*R*,5*E*)-2,5-bis(((*R*)-1-phenylethyl)imino)bicyclo[2.2.2]octane-1,4-dicarboxylate (2)



2

R_f (Pentane/EtOAc/NEt_3 92:7:1) = 0.48. **$[\alpha]_D^{20}$** = +47.2 (*c* = 1.00 in $CHCl_3$). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.35 – 7.18 (m, 10H, $CH_{arom.}$), 4.59 (q, 2H, *J* = 6.4 Hz, CH_2), 4.26 (q, 4H *J* = 7.1 Hz, CH_2), 3.10 (dd, 2H, *J* = 18.0, 2.1 Hz, C*H*H), 2.47 (d, 2H, *J* = 17.9 Hz,CH*H*), 2.32 – 2.23 (m, 2H, CH*H*), 1.81 – 1.72 (m, 2H, C*H*H), 1.37 (d, 6H, *J* = 6.5 Hz, CH_3), 1.30 (t, 6H, *J* = 7.1 Hz, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 172.3 (COO), 167.1 (C=N), 145.7 ($C_{q,arom.}$), 128.4 ($C_{arom.}H$), 126.7 ($C_{arom.}H$), 126.6 ($C_{arom.}H$), 61.0, 58.7, 53.0, 34.4, 25.8, 25.3, 14.4. **MS-ES-EM (pos.)**: calculated for $[C_{30}H_{36}N_2O_4H]^+$: m/z = 489.2748, found: m/z = 489.2745; calculated for $[C_{30}H_{36}N_2O_4Na]$+: m/z = 511.2567, found: m/z = 511.2567. **ATR-FTIR:** v/ cm^{-1} = 2974 (s), 1732 (m), 1667 (m), 1449 (s), 1280 (s), 1249 (m), 1068 (m), 700 (m).

1.2 Diethyl (1*R*,2*R*,4*R*,5*R*)-2,5-bis(((*R*)-1-phenylethyl)amino)bicyclo[2.2.2]octane-1,4-dicarboxylate (3)

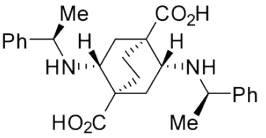


3

To diethyl (1R,2E,4R,5E)-2,5-bis(((R)-1-phenylethyl)imino)-bicyclo[2.2.2]octane-1,4-dicarboxylate (**2**) (1.21 g, 2.48 mmol, 1.0 equiv.) in EtOH (62 mL) at room-temperature was added $NaBH_4$ (3 x 0.28 g, 7.43 mmol, 3 equiv.) in 3 portions in 3 hour intervals. After 24 h, water (50 mL) was added and the mixture was neutralized with sulfuric acid (c = 3 mol/L). The product was extracted with CH_2Cl_2 (50 mL), the organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification via flash column chromatography (*n*-pentane/EtOAc 17:3) gave the product **3** as a colorless solid (0.32 g, 0.65 mmol, 26%).

R_f (Pentane/EtOAc 4:1) = 0.95. **$[\alpha]_D^{20}$** = −16.2 (*c* = 1.00 in $CHCl_3$). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.34 – 7.17 (m, 10H, $CH_{arom.}$), 4.12 (qd, 4H, *J* = 7.1, 0.7 Hz, CH_2), 3.71 (q, 2H, *J* = 6.5 Hz, C*H*N), 3.11 (dd, 2H, *J* = 9.6, 4.3 Hz, C*H*N), 2.18 – 2.09 (m, 2H, $CH_{(up)}H_{(down)}$), 2.05 – 2.01 (m, 2H, CH*H*), 1.70 - 166 (m, 2H, C*H*H), 1.28 (dd, 2H, *J* = 13.5, 4.6 Hz, $CH_{(up)}H_{(down)}$), 1.25 (t, 6H, *J* = 6.2 Hz, CH_3), 1.23 (d, 6H, *J* = 4.7 Hz, CH_3). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 176.1 (COO), 146.9 ($C_{q,arom}$), 128.5 ($C_{arom.}H$), 126.9 ($C_{arom.}H$), 126.6 ($C_{arom.}H$), 60.5 (CH_2), 55.9 (CH), 53.9 (CH), 45.2 (C_q), 39.4 (CH_2), 23.5 (CH_2), 21.1 (CH_2), 14.4 (CH_3). **MS-ES-EM (pos.)**: calculated for $[C_{30}H_{40}N_2O_4H]^+$: m/z = 493.3061, found: m/z = 493.3069, calculated for $[C_{30}H_{40}N_2O_4Na]^+$: m/z = 515.2886, found: m/z = 515.2864. **ATR-FTIR:** v/ cm^{-1} = 2972 (w), 1721 (m), 1451(s), 1366 (s), 1250 (m), 1073 (m), 762 (s), 702 (m), 632 (m).

1.3 (1*R*,2*R*,4*R*,5*R*)-2,5-Bis(((*R*)-1-phenylethyl)amino)bicyclo[2.2.2]octane-1,4-dicarboxylic acid (H_2L)



H_2L

To (1*R*,2*R*,4*R*,5*R*)-diethyl-2,5-bis-(((*R*)-1-phenylethyl)-amino) bicyclo[2.2.2]octan-1,4-di-carboxylate (**3**) (1.69 g, 3.43 mmol, 1.0 equiv.) dissolved in EtOH/H_2O (1:1, 200 mL) was added NaOH (4.12 g, 103 mmol, 30 equiv.) and stirred at 60 °C for 24 h. The solvent was removed under reduced pressure and the residual solution was neutralized with H_2SO_4. The aqueous phase was washed with *i*PrOH/$CHCl_3$ and the water was removed by lyophilization. The solid residue was taken up in EtOH, filtered and the filtrate was concentrated to dryness to give the product **H_2L** as a white powder (1.29 g, 2.96 mmol, 86%).

$[\alpha]_D^{20}$ = −102.3 (*c* = 1.00 in MeOH). **^{1}H NMR** (400 MHz, CD_3OD): δ = 7.53 – 7.41 (m, 10H, $CH_{arom.}$), 4.33 (q, 2H, *J* = 6.8 Hz, CH), 3.48 (t, 2H, *J* = 7.9 Hz, C*H*N), 1.95 – 1.74 (m, 8H 4x CH*H*), 1.66 (d, 6H, *J* = 6.8 Hz, 2x CH_3). **^{13}C NMR** (100 MHz, CD_3OD): δ = 180.9 (COO), 139.2 ($C_{q,arom.}$), 130.5 ($C_{arom}H$), 128.6 ($C_{arom.}H$), 58.6 (CH), 55.9 (CH), 53.9 (C*H*N), 41.4 (C_q) 34.5 (CH*H*), 24.3 (C*H*H), 19.7 (CH_3). **MS-ES-EM (pos.)**: calculated for $[C_{26}H_{32}N_2O_4H]^+$: m/z = 437.2435, found: m/z = 437.2428, calculated for $[C_{26}H_{32}N_2O_4Na]^+$: m/z = 459.2254, found:

m/z = 459.2248. **ATR-FTIR:** v / cm-1 = 2978 (w), 2871 (w), 1600 (m), 1494 (s), 1453(m), 1383 (m), 1250 (m), 1212 (m), 1065 (s), 917 (m), 762 (m), 700 (m), 621 (s).

Diethyl (1*S*,2*E*,4*S*,5*E*)-2,5-bis(((*R*)-1-phenylethyl)imino)bicyclo[2.2.2]octane-1,4-dicarboxylate (**1**) was also used as starting reagent for the synthesis of bicyclo[2.2.2]octane-1,4-dicarboxylate based linker, whereas the synthetic procedure was identical to that applied to **2** (steps 1.2 – 1.3). The linker was utilized under synthetic conditions of DUT-129 yielding amorphous product.

2. NMR Spectra

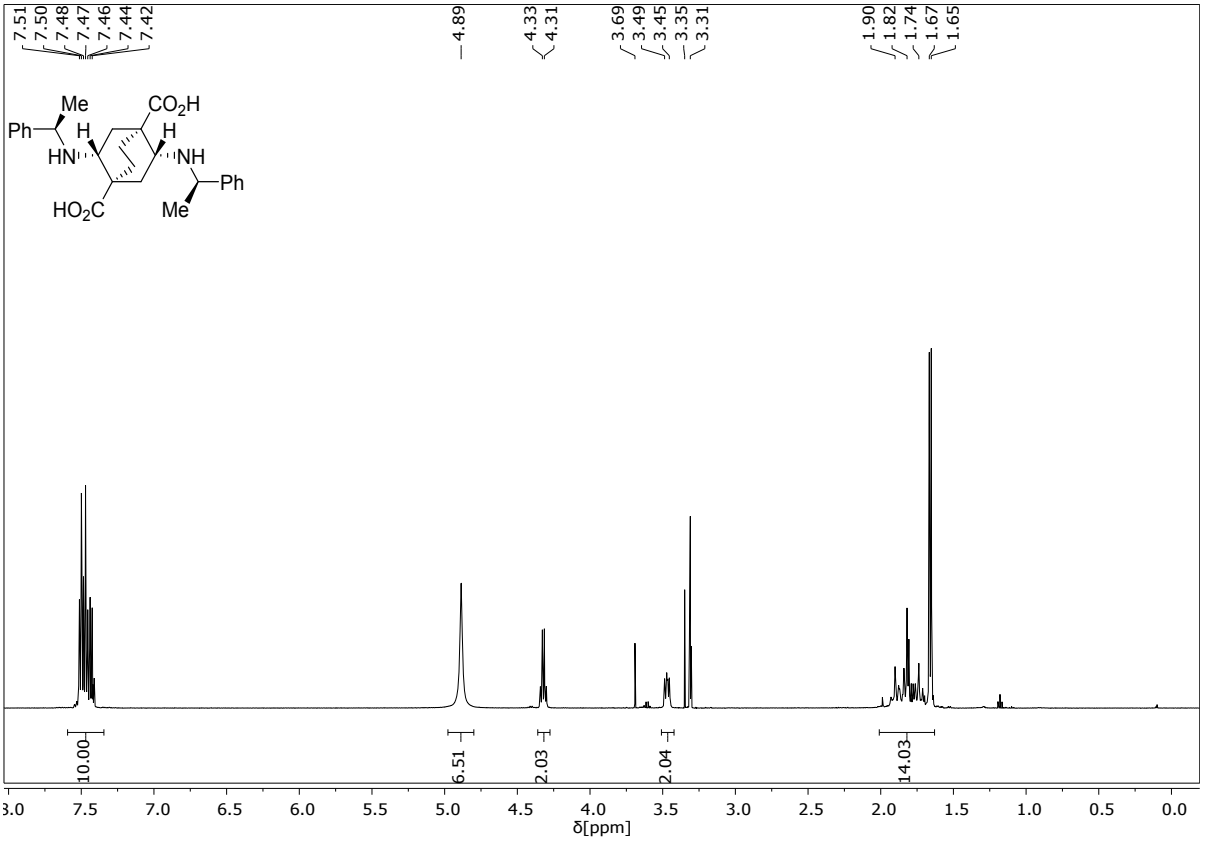
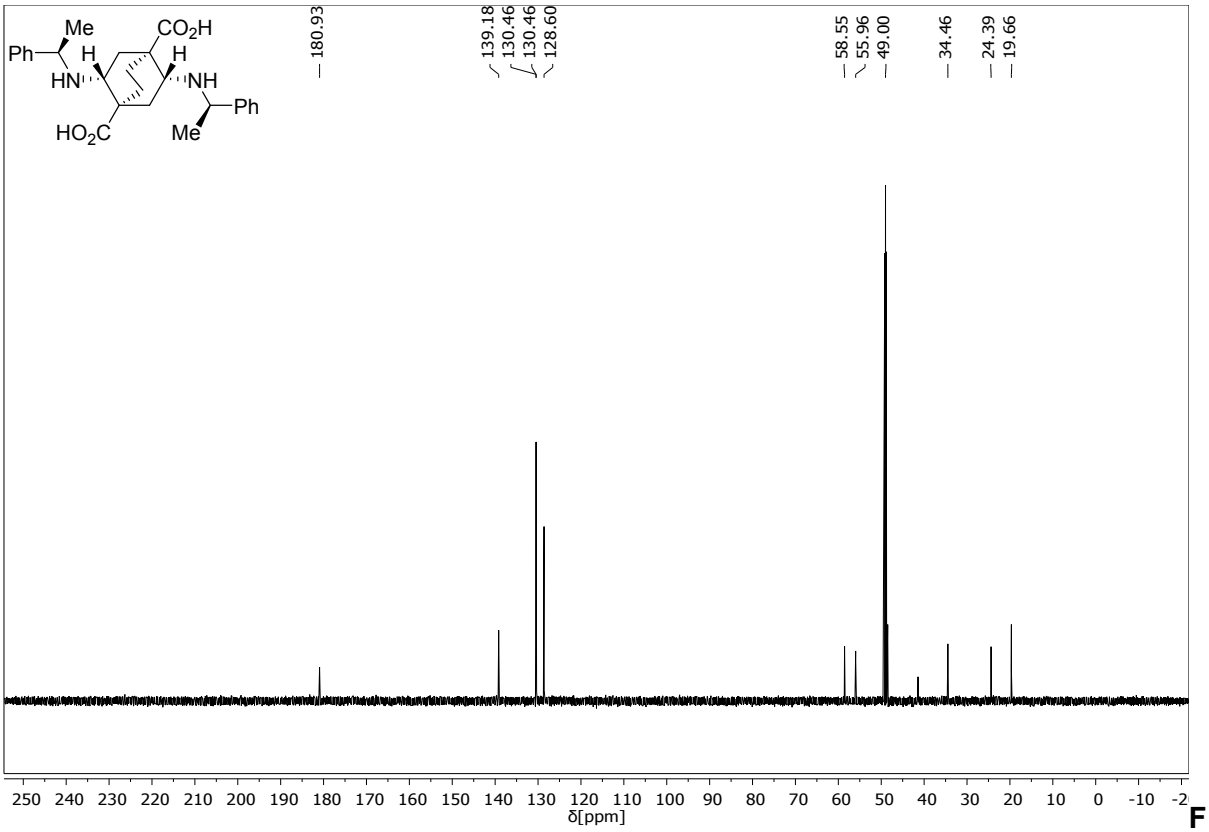


Figure S1. ^{1}H NMR spectra of H_2**L** in $(CD_3)OD$.



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igure S2. ^{13}C NMR spectra of H_2**L** in $(CD_3)OD$.

3. PXRD Analysis

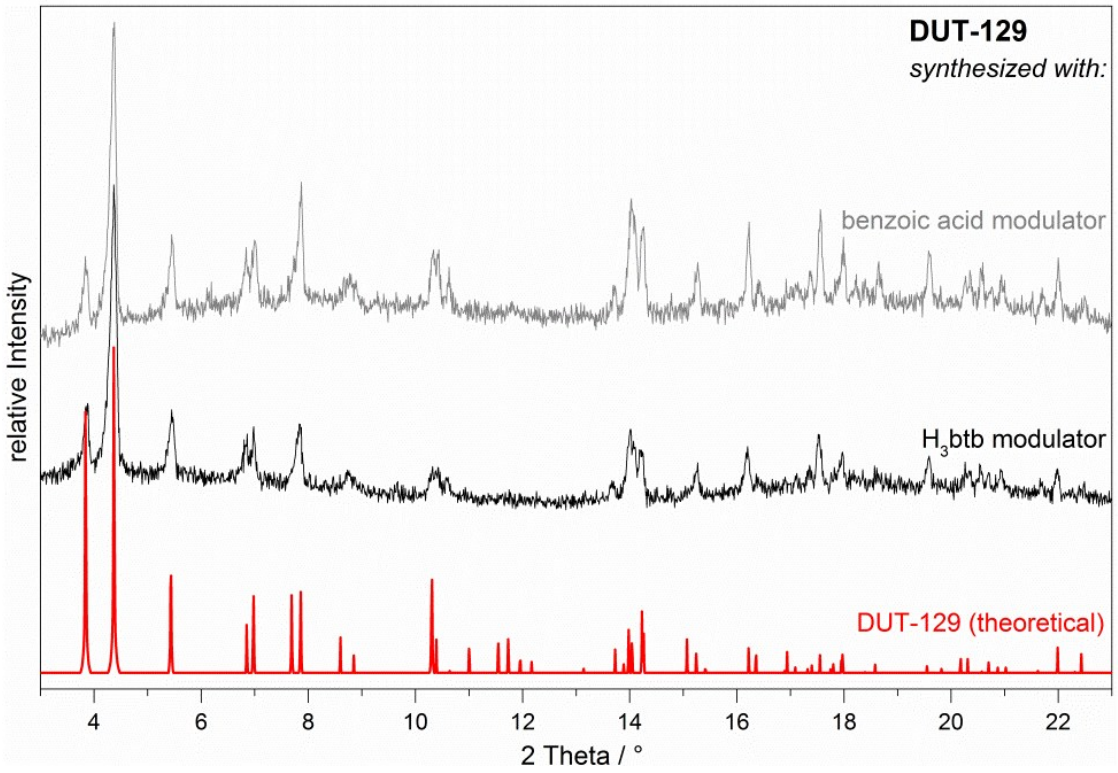


Figure S3. PXRD patterns of DUT-129 synthesized using different modulators: Benzoic acid (grey) and H_3btb (black) compared to the calculated (red) PXRD pattern.

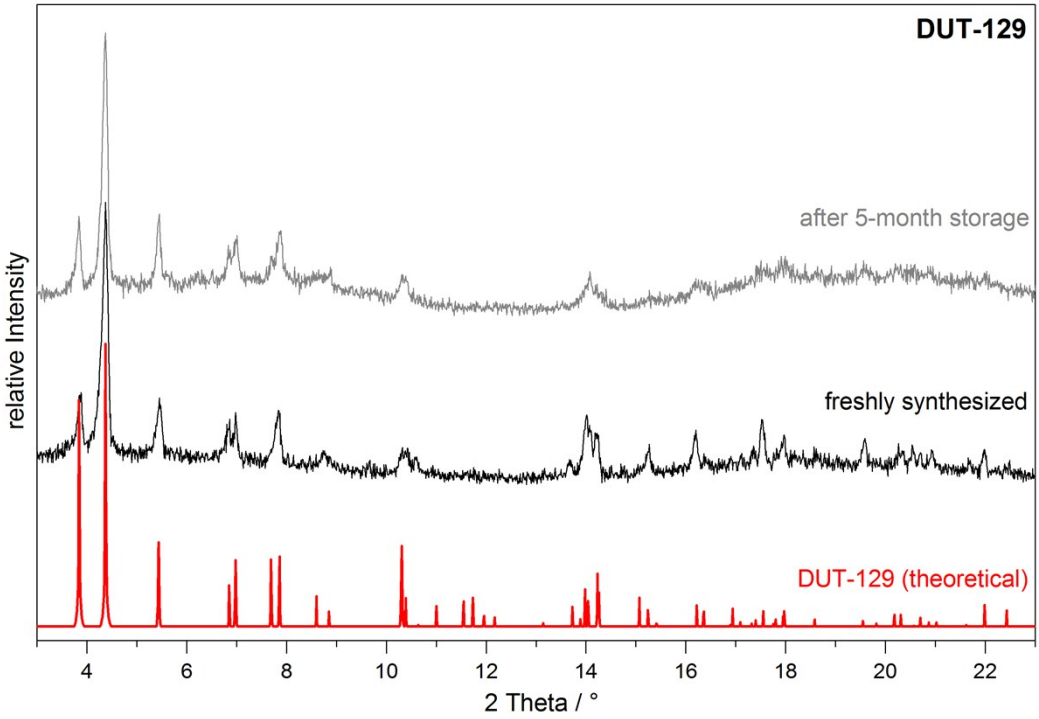


Figure S4. PXRD patterns of DUT-129 directly after synthesis (black) and after 5-month storage (grey) in comparison to the theoretical pattern (red).

4. Adsorption experiments

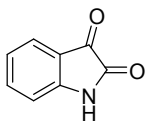
For activation of the MOF DUT-129 three different procedures were tested:

a) Conventional drying procedure from ethanol: The as made material was washed with ethanol (5 x 3 mL) and the remaining solvent was removed. The material was dried in high vacuum at room temperature.
b) Super critical drying (SCD) from ethanol: The solvent of the prepared sample was exchanged by ethanol (3 x 5 mL) and furthermore several times by liquid CO_2 over a period of 3 days. The CO_2 was finally transformed into supercritical state and slowly released from the apparatus. The dried material was stored in inert gas atmosphere.

Nitrogen physisorption measurements were performed using a BELSORP MAX system from BEL JAPAN, INC. Analysis temperature was 77 K and samples were additionally activated in high vacuum at room temperature for 18 h prior to measurements.

Materials showed no uptake of nitrogen indicating absence of porosity in activated state. PXRD analysis of the activated samples showed amorphous character of the samples after activation.

Adsorption of isatin from ethanol. Analysis of the crystal structure shows, that the pore windows are 5.2 Å in diameter. Therefore, a small dye, isatin, was chosen to investigate the pore accessibility. A solution of isatin (5.9 mg, 0.04 mmol) in ethanol (40 mL) was prepared. The as-synthesized DUT-129 material was washed with ethanol (3 x 5 mL) and the remaining solvent was removed. For adsorption experiments, the yellow dye solution (1 mL) was added to the MOF sample but the white powder did not change the color after 4 days.



Isatin

5. References

[1] E. Weber, M. Hecker, E. Koepp, W. Orlia, *J. Chem. Soc. PERKIN TRANS II*, **1988**, 1251-1257.