Electronic supporting information

Synthesis and post-synthetic modification of amine-, alkyne-, azide- and nitro-functionalized metal-organic frameworks based on DUT-5

Meike A. Gotthardt[a], Sylvain Grosjean[b,c], Tobias S. Brunner[d], Johannes Kotzel[a], Andreas M. Gänzler[a], Silke Wolf[d], Stefan Bräse*[b,e], Wolfgang Kleist*[a,f]

[a] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 20, 76131 Karlsruhe, Germany

[b] Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany, tel.: 0049 721 60842903, fax: 0049 721 60848581, e-mail address: stefan.braese@kit.edu

[c] Soft Matter Synthesis Lab, Institute for Biological Interfaces, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

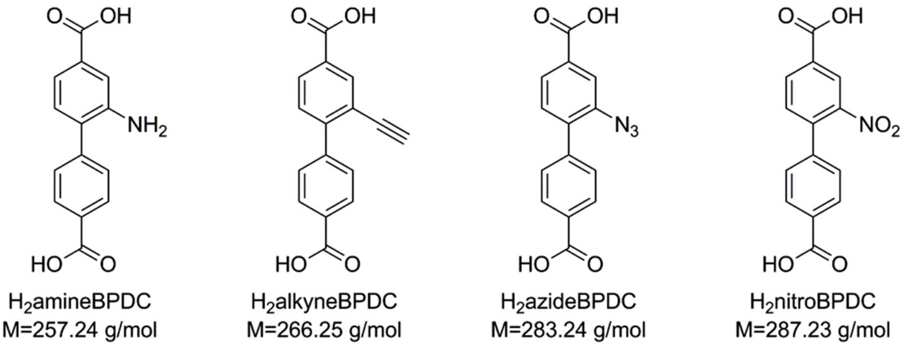
[d] Institute for Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany

[e] Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[f] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, tel.: 0049 721 60847989, fax: 0049 721 60844820, e-mail address: wolfgang.kleist@kit.edu

Table of contents

1. Synthesis of functionalized 4,4’-biphenyldicarboxylic acid molecules



Scheme S1. Structures of 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2amineBPDC, left), 2-ethynyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2alkyneBPDC, middle left), 2-azido-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2azideBPDC, middle right) and 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2nitroBPDC, right).

General methods

All applied reagents and solvents were commercially available and used as supplied without further purification. Functionalized biphenyldicarboxylic acid (BPDC) derivatives and precursors were characterized with nuclear magnetic resonance (NMR) spectroscopy, high resolution mass spectrometry (HRMS), and infra-red spectroscopy (IR). NMR spectra were recorded on a Bruker AM 500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) as solutions in $CDCl_3$ or in DMSO-d_6. Chemical shifts δ were quoted in parts per million (ppm) and were referenced to residual solvent peaks as internal standard. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet and m = multiplet. Coupling constants J are reported in Hertz (Hz). Mass spectra were recorded with a Finnigan MAT 95 (70 eV) spectrometer under electron impact (EI) conditions. The molecular fragments were quoted as the relation between mass and charge (*m/z*). The abbreviation [M^+] refers to the molecular ion. IR spectra were recorded with a FTIR Bruker IFS 88 spectrometer, using the attenuated total reflection technique (ATR). The absorption band positions are given in wave numbers ν in cm^{-1}.

Synthesis of 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2nitroBPDC), 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2amineBPDC), 2-azido-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2azideBPDC) and 2-ethynyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2alkyneBPDC)

The key intermediates dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (1) and dimethyl 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylate (2) were prepared via a literature procedure.[1]

2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2nitroBPDC)[2]: Dimethyl 2-nitrobiphenyl-dicarboxylate (1) (0.25 g, 0.79 mmol, 1 equiv.) was suspended in tetrahydrofuran (THF, 10 mL). A solution of potassium hydroxide (0.27 g, 4.76 mmol, 6 equiv.) in water (6 mL) was added and the reaction mixture was refluxed for 20 h. THF was evaporated under reduced pressure and 6M HCl was added (pH = 1). The aqueous suspension was filtrated, the solid washed with water and methanol and dried under vacuum to give (H_2nitroBPDC) as a pale yellow solid (0.17 g, 74%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 13.44 (br-s, 2H, CO_2H), 8.47 (d, 1H, J = 1.5 Hz, CH_{Ar}), 8.28 (dd, 1H, J = 8.0 Hz, J = 1.5 Hz, CH_{Ar}), 8.03 (d, 2H, J = 8.0 Hz, CH_{Ar}), 7.73 (d, 1H, J = 8.0 Hz, CH_{Ar}), 7.52 (d, 2H, J = 8.0 Hz, CH_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 166.9 (CO_2H), 165.3 (CO_2H), 148.5 (C^{IV}_{Ar}), 140.7 (C^{IV}_{Ar}), 138.3 (C^{IV}_{Ar}), 133.3 (CH_{Ar}), 132.6 (CH_{Ar}), 131.8 (C^{IV}_{Ar}), 130.9 (C^{IV}_{Ar}), 129.7 (CH_{Ar}), 128.1 (CH_{Ar}), 125.3 (CH_{Ar}) ppm. ATR-IR: ν = 1690, 1607, 1534, 1423, 1344, 1284, 1129 cm^{-1}. EI-MS: m/z = 287 [M^+]. EI-HRMS: m/z $C_{14}H_9NO_6$, calcd.: 287.0430, found: 287.0422.

2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2aminoBPDC)[3]: Dimethyl 2-aminobiphenyldicarboxylate (2) (1.00 g, 3.51 mmol, 1 equiv.) was suspended in THF (30 mL). A solution of potassium hydroxide (1.18 g, 21.03 mmol, 6 equiv.) in water (20 mL) was added and the reaction mixture was refluxed for 20 h. THF was evaporated under reduced pressure and 6M HCl was added (pH = 1). The aqueous suspension was filtrated, the solid washed with water and methanol and dried under vacuum to give (H_2aminoBPDC) as a pale yellow solid (0.86 g, 95%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 13.04 (br-s, 2H, CO_2H), 8.03 (d, 2H, J = 7.5 Hz, CH_{Ar}), 7.67 (s, 1H, CH_{Ar}), 7.63 (d, 2H, J = 7.5 Hz, CH_{Ar}), 7.49 (d, 1H, J = 8.0 Hz, CH_{Ar}), 7.28 (d, 1H, J = 8.0 Hz, CH_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO- d_6): δ = 167.1 (CO_2H), 167.0 (CO_2H), 142.3 (C^{IV}_{Ar}), 140.3 (C^{IV}_{Ar}), 132.1 (C^{IV}_{Ar}), 131.2 (C^{IV}_{Ar}), 130.8 (CH_{Ar}), 130.0 (C^{IV}_{Ar}), 129.8 (CH_{Ar}), 129.0 (CH_{Ar}), 121.3 (CH_{Ar}), 119.3 (CH_{Ar}) ppm. ATR-IR: ν = 3349, 1678, 1606, 1430, 1392, 1234, 1114 cm^{-1}. EI-MS: m/z = 257 [M^+]. EI-HRMS: m/z $C_{14}H_{11}NO_4$, calcd.: 257.0688, found: 257.0681.

2-azido-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2azidoBPDC)[4]: 2-aminobiphenyl dicarboxylic acid (H_2aminoBPDC) (0.40 g, 1.56 mmol, 1 equiv.) was dissolved in dry THF (45 mL) and *tert*-butyl nitrite (0.56 mL, 4.67 mmol, 3 equiv.) was added at 0 °C. After stirring for 15 min trimethylsilylazide (0.41 mL, 3.11 mmol, 2 equiv.) was added at 0 °C, the reaction mixture was slowly warmed-up to room temperature and stirred for 48 h. The reaction mixture was evaporated under reduced pressure, the solid was treated with cold THF, filtrated and dried under vacuum to give (H_2azidoBPDC) as a yellow-white solid (0.43 g, 97%). ^{1}H-NMR (500 MHz, DMSO- d_6): δ = 13.22 (b-s, 2H, CO_2H), 8.02 (d, 2H, J = 7.5 Hz, CH_{Ar}), 7.85-7.81 (m, 2H, CH_{Ar}), 7.64 (d, 2H, J = 7.5 Hz, CH_{Ar}), 7.56 (d, 1H, J = 7.5 Hz, CH_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO- d_6): δ = 167.0 (CO_2H), 166.3 (CO_2H), 141.1 (C^{IV}_{Ar}), 137.2 (C^{IV}_{Ar}), 135.7 (C^{IV}_{Ar}), 131.9 (C^{IV}_{Ar}), 131.4 (CH_{Ar}), 130.2 (C^{IV}_{Ar}), 129.6 (CH_{Ar}), 129.2 (CH_{Ar}), 125.9 (CH_{Ar}), 119.9 (CH_{Ar}) ppm. ATR-IR: ν = 2119, 1684, 1556, 1493, 1394, 1279 cm^{-1}. EI-MS: *m/z* = 283 [M$^+$], 255 [M$^+$-N_2]. EI-HRMS: *m/z* $C_{14}H_9N_3O_4$, calcd.: 283.0593, found: 283.0586.

Dimethyl 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylate (3)[1]: Dimethyl 2-aminobiphenyl dicarboxylate (2) (1.43 g, 5.00 mmol, 1 equiv.) was suspended in 15 % HCl (10 mL), the suspension was cooled to 0 °C and a solution of sodium nitrite (0.40 g, 5.75 mmol, 1.15 equiv.) in water (3 mL) was added drop wise. The mixture was stirred at 0 °C for 10 min and then a solution of sodium iodide (0.90 g, 6.00 mmol, 1.2 equiv.) in water (3 mL) was added drop wise. The resulting solution was heated to 60 °C for 20 min. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 x 250 mL). The combined organic phases were washed with a 10 % sodium sulfite solution and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified with column chromatography (silica gel, toluene) to give (3) as a white solid (1.27 g, 64%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.62 (s, 1H, CH_{Ar}), 8.12 (d, 2H, J = 8.5 Hz, CH_{Ar}), 8.06 (d, 1H, J = 8.0 Hz, CH_{Ar}), 7.42 (d, 2H, J = 8.5 Hz, CH_{Ar}), 7.35 (d, 1H, J = 8.0 Hz, CH_{Ar}), 3.95 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.9 (CO_2CH_3), 165.5 (CO_2CH_3), 150.1 (C^{IV}_{Ar}), 147.8 (C^{IV}_{Ar}), 140.9 (CH_{Ar}), 131.1 (C^{IV}_{Ar}), 130.0 (C^{IV}_{Ar}), 129.8 (CH_{Ar}), 129.6 (CH_{Ar}), 129.4 (CH_{Ar}), 129.3 (CH_{Ar}), 97.5 (C^{IV}_{Ar}-I), 52.6 (CO_2CH_3), 52.4 (CO_2CH_3) ppm. ATR-IR: ν = 2950, 1717, 1592, 1435, 1372, 1273, 1195 cm^{-1}. EI-MS: *m/z* = 396 [M$^+$], 365 [M$^+$-OCH_3]. EI-HRMS: *m/z* $C_{16}H_{13}IO_4$, calcd.: 395.9859, found: 395.9855.

Dimethyl 2-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (4): Dimethyl 2-iodobiphenyl dicarboxylate (3) (1.00 g, 2.52 mmol, 1 equiv.), copper iodide (24 mg, 0.13 mmol, 0.05 equiv.) and bis(triphenylphosphine)palladium(II) chloride (53 mg, 0.08 mmol, 0.03 equiv.) were dissolved in a mixture of THF and triethylamine (1:1, 50 mL) under argon atmosphere.

Trimethylsilylacetylene (1.05 mL, 7.57 mmol, 3 equiv.) was added and the mixture was stirred under argon atmosphere at room temperature for 24 h. The reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 200 mL). The organic phase was washed with water and brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, dichloromethane / n-hexane, $R_{f(DCM/nHx:7/3)}$ = 0.27) to give (4) (0.84 g, 91%) as a yellow-white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.26 (d, 1H, J = 1.5 Hz, CH_{Ar}), 8.09 (d, 2H, J = 8.0 Hz, CH_{Ar}), 8.03 (dd, 1H, J = 8.0 Hz, J = 1.5 Hz, CH_{Ar}), 7.70 (d, 2H, J = 8.0 Hz, CH_{Ar}), 7.45 (d, 1H, J = 8.0 Hz, CH_{Ar}), 3.95 (s, 3H, CO_2CH_3), 3.94 (s, 3H, CO_2CH_3), 0.14 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.0 (CO_2CH_3), 166.3 (CO_2CH_3), 147.1 (C^{IV}_{Ar}), 144.0 (C^{IV}_{Ar}), 134.9 (CH_{Ar}), 129.8 (C^{IV}_{Ar}), 129.7 (CH_{Ar}), 129.6 (CH_{Ar}), 129.6 (C^{IV}_{Ar}), 129.5 (CH_{Ar}), 129.3 (CH_{Ar}), 122.0 (C^{IV}_{Ar}-C≡CTMS), 103.2 (ArC≡CTMS), 99.5 (ArC≡CTMS), 52.5 (CO_2CH_3), 52.4 (CO_2CH_3), -0.3 ($Si(CH_3)_3$) ppm. ATR-IR: ν = 2948, 2896, 2155, 1715, 1605, 1431, 1386, 1278, 1185 cm^{-1}. EI-MS: m/z = 366 [M^+], 351 [M^+-CH_3], 335 [M^+-OCH_3]. EI-HRMS: m/z $C_{21}H_{22}O_4Si$, calcd.: 366.1287, found: 366.1282.

2-ethynyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2alkyneBPDC): Dimethyl 2-((trimethylsilyl)ethynyl)biphenyl dicarboxylate (4) (0.50 g, 1.36 mmol, 1 equiv.) was dissolved in THF (20 mL). A solution of potassium hydroxide (0.77 g, 13.64 mmol, 10 equiv.) in water (15 mL) was added and the reaction mixture was stirred at room temperature for 72 h. THF was evaporated under reduced pressure and 6M HCl was added (pH = 1). The brown-yellow milky suspension was extracted with ethyl acetate (3 x 150 mL). The combined organic phases were washed with water and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give (H_2alkyneBPDC) as a yellow-white solid (0.33 g, 92%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 13.19 (b-s, 2H, CO_2H), 8.10 (s, 1H, CH_{Ar}), 8.04-8.03 (m, 3H, CH_{Ar}), 7.72 (d, 2H, J = 8.0 Hz, CH_{Ar}), 7.61 (d, 1H, J = 8.0 Hz, CH_{Ar}), 4.29 (s, 1H, ArC≡CH) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 167.0 (CO_2H), 166.2 (CO_2H), 146.3 (C^{IV}_{Ar}), 143.0 (C^{IV}_{Ar}), 134.3 (CH_{Ar}), 130.5 (C^{IV}_{Ar}), 130.1 (CH_{Ar}), 129.9 (CH_{Ar}), 129.3 (CH_{Ar}), 129.2 (CH_{Ar}), 120.4 (C^{IV}_{Ar}-C≡CH), 84.8 (ArC≡CH), 81.6 (ArC≡CH) ppm. ATR-IR: ν = 3279, 1678, 1599, 1572, 1420, 1289, 1191 cm^{-1}. EI-MS: m/z = 266 [M^+], 249 [M^+-OH]. EI-HRMS: m/z $C_{16}H_{10}O_4$, calcd.: 266.0579, found: 266.0575.

2. Synthesis of functionalized metal-organic frameworks DUT-5

0.54 mmol of the functionalized biphenyl-4,4’-dicarboxylic acid molecules (see Table S1) were dissolved in 20 mL *N,N*-dimethylformamide (DMF) at 120 °C. A solution of 0.2600 g (0.70 mmol) aluminum nitrate nonahydrate ($Al(NO_3)_3*9H_2O$) in 5 mL DMF was added. The reaction mixture was stirred for 24 h under reflux at 120 °C. After filtration the metal-organic frameworks were washed with 3 x 25 mL of DMF and 1 x 25 mL of H_2O. The solid was dried over night at room temperature and then for 3 days at 130 °C. Theoretical yields for dry materials [Al(OH)(functionalizedBPDC)] and actual yields for the functionalized frameworks containing water and traces of residual DMF are listed in Table S2.

Table S1. Mass of linker molecules applied in the synthesis of functionalized DUT-5.

linker molecule	acronym	mass [g]
2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid	H_2amineBPDC	0.1377
2-ethynyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid	H_2alkyneBPDC	0.1425
2-azido-[1,1'-biphenyl]-4,4'-dicarboxylic acid	H_2azideBPDC	0.1516
2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylic acid	H_2nitroBPDC	0.1537

Table S2. Theoretical yields of dry DUT-5 materials and actual yields of materials containing water and traces of residual solvent (DMF).

material	theoretical yield of dry MOF [g]	actual yield of MOF with H_2O/DMF [g]
DUT-5	0.153	0.155
DUT-5-amine	0.161	n.d.
DUT-5-alkyne	0.166	0.180
DUT-5-azide	0.176	n.d.
DUT-5-nitro	0.178	0.150

3. Synthesis of mixed-linker metal-organic frameworks MIXDUT-5

0.54 mmol of the linker molecules (defined ratios of biphenyl-4,4’-dicarboxylic acid and functionalized biphenyl-4,4’-dicarboxylic acid, Table S3) were dissolved in 20 mL DMF at 120 °C. A solution of 0.2600 g (0.70 mmol) $Al(NO_3)_3*9H_2O$ in 5 mL DMF was added. The reaction mixture was stirred for 24 h under reflux at 120 °C. After filtration the metal-organic frameworks were washed with 3 x 25 mL of DMF and 1 x 25 mL of H_2O. The solid was dried over night at room temperature and then for 3 days at 130 °C. Theoretical yields for dry materials $[Al(OH)(BPDC)_{1-x}(\text{functionalizedBPDC})_x]$ and actual yields for the mixed-linker metal-organic frameworks containing water and traces of residual DMF are listed in Table S4.

Table S3. Ratios and masses of linker molecules applied in the synthesis of MIXDUT-5 frameworks.

linker molecules	ratio	acronym	masses [g]
H_2BPDC : H_2amineBPDC	3 : 1	MIXDUT-5-amine(25)	0.0972 : 0.0344
H_2BPDC : H_2amineBPDC	1 : 1	MIXDUT-5-amine(50)	0.0648 : 0.0688
H_2BPDC : H_2amineBPDC	1 : 3	MIXDUT-5-amine(75)	0.0324 : 0.1032
H_2BPDC : H_2alkyneBPDC	3 : 1	MIXDUT-5-alkyne(25)	0.0972 : 0.0356
H_2BPDC : H_2alkyneBPDC	1 : 1	MIXDUT-5-alkyne(50)	0.0648 : 0.0712
H_2BPDC : H_2alkyneBPDC	1 : 3	MIXDUT-5-alkyne(75)	0.0324 : 0.1069
H_2BPDC : H_2nitroBPDC	1 : 1	MIXDUT-5-nitro(50)	0.0654 : 0.0776
H_2BPDC : H_2azideBPDC	1 : 1	MIXDUT-5-azide(50)	0.0648 : 0.0758
H_2BPDC : H_2amineBPDC : H_2alkyneBPDC	1 : 1 : 1	MIXDUT-5- amine(33)-alkyne(33)	0.0432 : 0.0459 : 0.0475

Table S4. Theoretical yields of dry MIXDUT-5 materials and actual yields of materials containing water and traces of residual solvent (DMF).

material	theoretical yield of dry MOF [g]	actual yield of MOF with H_2O/DMF [g]
MIXDUT-5-amine(25)	0.155	n.d.
MIXDUT-5-amine(50)	0.157	0.165
MIXDUT-5-amine(75)	0.159	n.d.
MIXDUT-5-alkyne(25)	0.156	0.160
MIXDUT-5-alkyne(50)	0.160	0.150
MIXDUT-5-alkyne(75)	0.163	0.080
MIXDUT-5-azide(50)	0.165	n.d.
MIXDUT-5-nitro(50)	0.166	0.120
MIXDUT-5-amine(33)-alkyne(33)	0.160	n.d.

4. Post-synthetic modification (PSM)

4.1 MIXDUT-5-amine(50)-Mal

0.3922 g maleic anhydride (4 mmol, 8 equiv.) were dissolved in 25 mL acetonitrile and 0.2917 g (1 mmol, 1 equiv.) of freshly dried MIXDUT-5-amine(50) were suspended in the solution. The reaction mixture was then heated under reflux to 80 °C for 24 h. After filtration the modified framework was washed with 4 x 20 mL acetonitrile, 1 x 20 mL DMF and 1 x 20 mL H_2O. The solid was dried over night at room temperature and then for 3 days at 130 °C in air.

4.2 MIXDUT-5-amine(50)-Sal

1.2213 g salicylaldehyde (10 mmol, 20 equiv.) were dissolved in 25 mL toluene and 0.2917 g (1 mmol, 1 equiv.) of freshly dried MIXDUT-5-amine(50) were suspended in the solution. The reaction mixture was then heated under reflux to 100 °C for 72 h. After filtration the modified framework was washed with 5 x 25 mL toluene. The solid was dried over night at room temperature and then for 3 days at 130 °C in air.

4.3 MIXDUT-5-amine(50)-Pyal

1.0711 g 2-pyridinecarboxaldehyde (10 mmol, 20 equiv.) were dissolved in 25 mL toluene and 0.2917 g (1 mmol, 1 equiv.) of freshly dried MIXDUT-5-amine(50) were suspended in the solution. The reaction mixture was then heated under reflux to 100 °C for 72 h. After filtration the modified framework was washed with 5 x 25 mL toluene. The solid was dried over night at room temperature and then for 3 days at 130 °C in air.

4.4 MIXDUT-5-alkyne(50)-Pyaz

0.0505 g 2-pyridine azide (0.42 mmol), 0.0208 g $CuSO_4*5H_2O$ (0.08 mmol) and 0.0165 g sodium ascorbate (0.08 mmol) were dissolved in 20 mL DMF and 0.2962 g (1 mmol) of freshly dried MIXDUT-5-alkyne(50) were suspended in the solution. The reaction mixture was then left at room temperature for 24 h. After filtration the modified framework was washed with 1 x 10 mL DMF, 5 x 10 mL H_2O and 10 mL DCM. The solid was dried over night at room temperature and then for 3 days at 130 °C in air.

5. X-ray diffraction measurements (XRD)

Powder X-ray diffraction measurements were performed using a Bruker D8 Advance. The samples were analyzed in the range 2 Θ = 4 - 50° using Cu Kα radiation. The step width was 2 Θ = 0.0164° with a dwell time of 2 s.

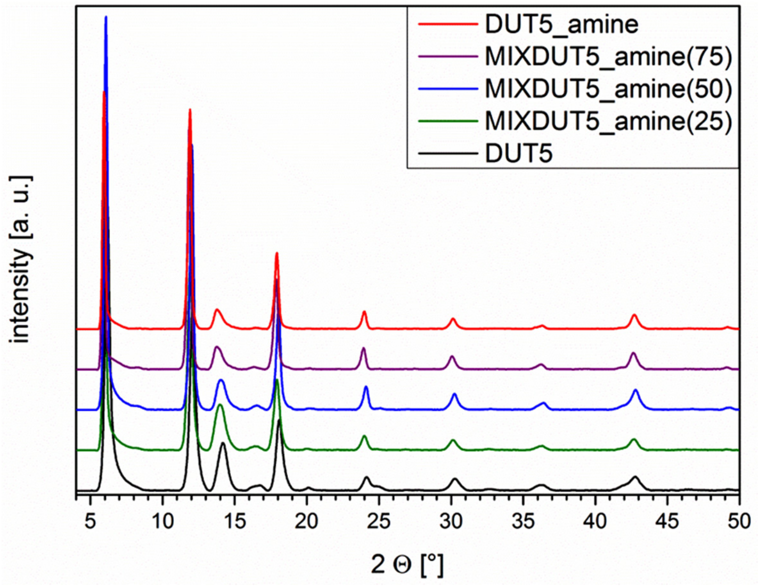


Figure S1. X-ray diffraction patterns of DUT-5 (black), DUT-5-amine (red) and MIXDUT-5-amine(x) (x=75, purple; x=50, blue; x=25, green).

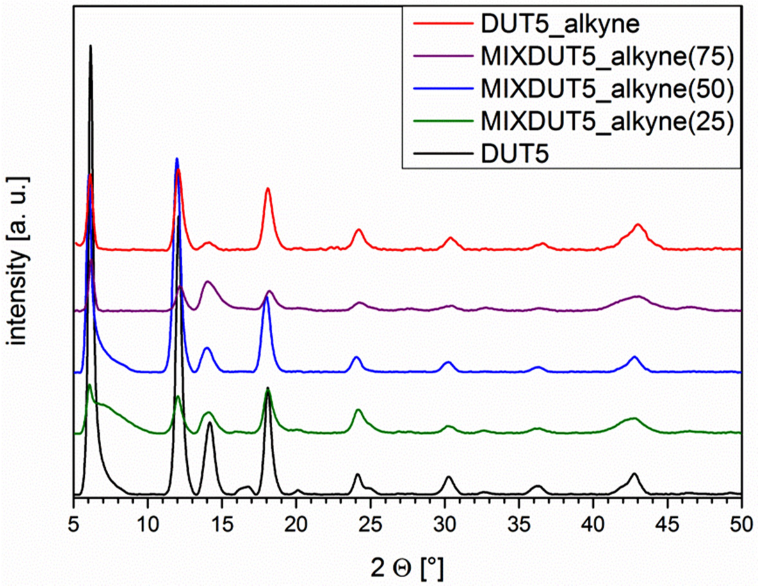


Figure S2. X-ray diffraction patterns of DUT-5 (black), DUT-5-alkyne (red) and MIXDUT-5-alkyne(x) (x=75, purple; x=50, blue; x=25, green).

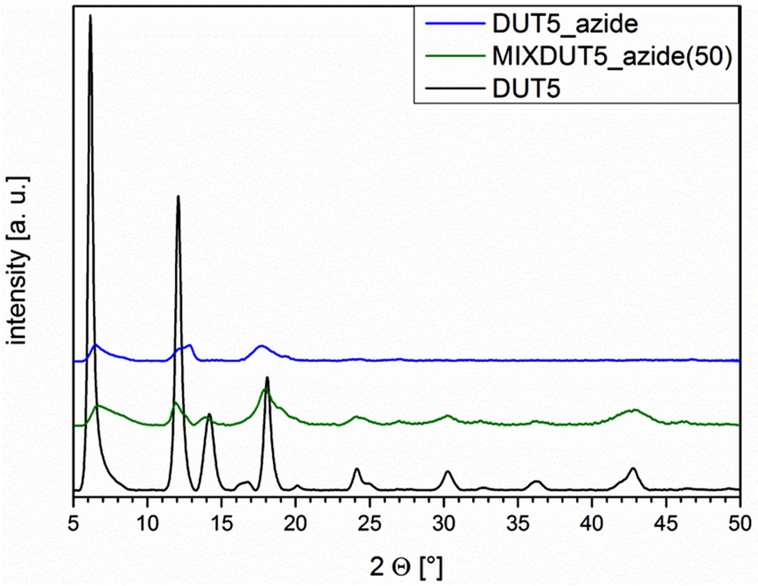


Figure S3. X-ray diffraction patterns of DUT-5 (black), DUT-5-azide (blue) and MIXDUT-5-azide(50) (green).

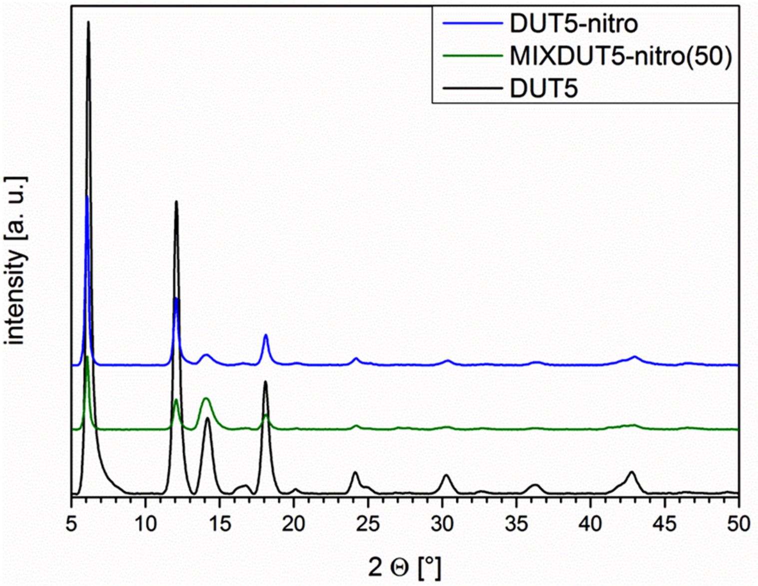


Figure S4: X-ray diffraction patterns of DUT-5 (black) and MIXDUT-5-nitro(50) (green).

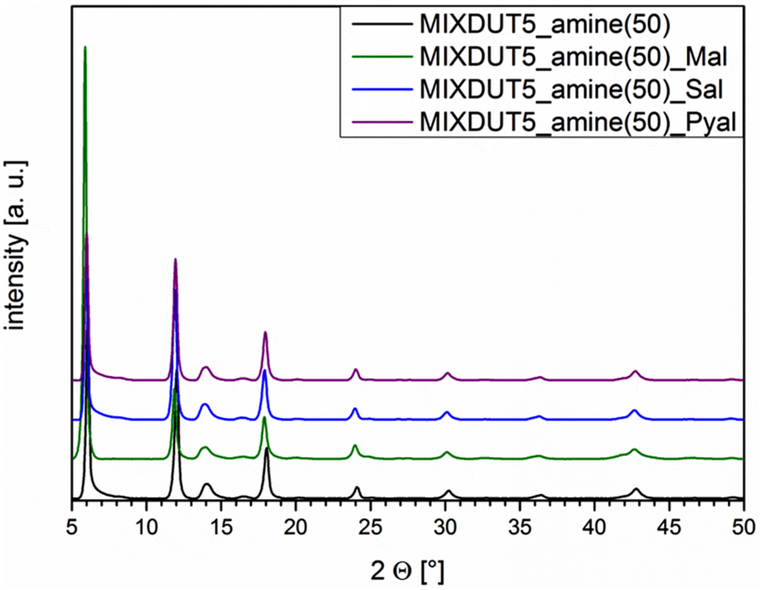


Figure S5. X-ray diffraction patterns of MIXDUT-5-amine(50) (black), MIXDUT-5-amine(50)-Mal (green), MIXDUT-5-amine(50)-Sal(blue) and MIXDUT-5-amine(50)-Pyal (purple).

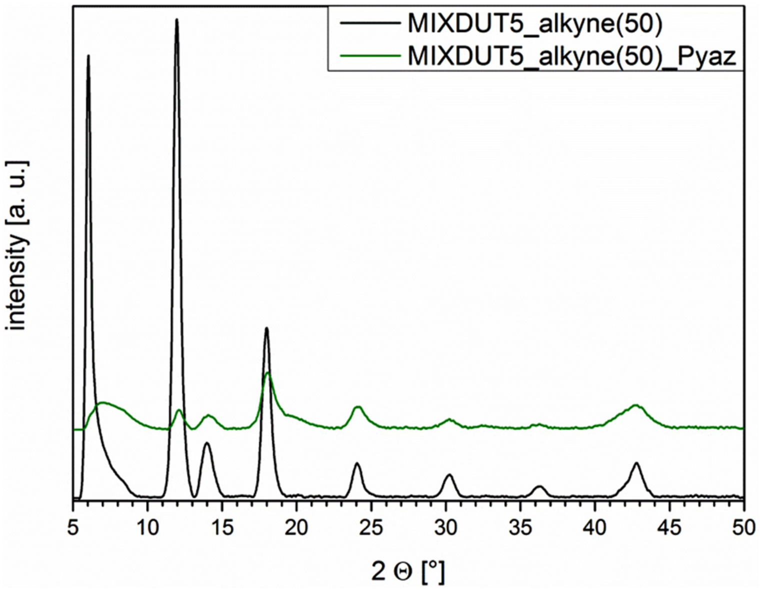


Figure S6. X-ray diffraction patterns of MIXDUT-5-alkyne(50) (black) and MIXDUT-5-alkyne(50)-Pyaz (green).

6. Attenuated total reflection infrared spectroscopy (ATR-IR)

IR data were acquired using a FT-IR spectrometer Vertex 70 from Bruker Optics equipped with a Golden Gate Single Reflection ATR sample cell from Specac. The data were collected from 4500 to 600 cm^{-1} and for each spectrum the arithmetic average of 400 measurements was taken.

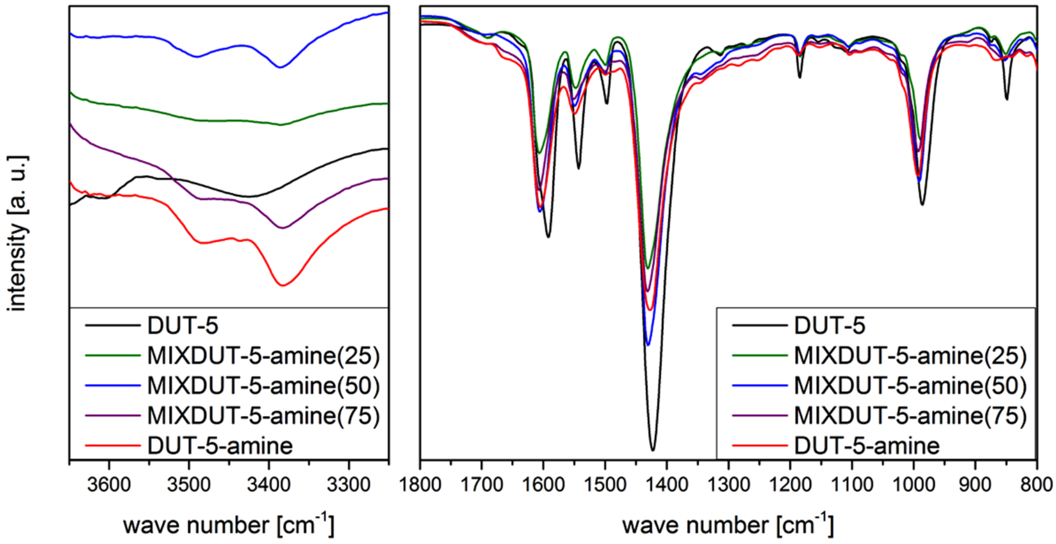


Figure S7: ATR-IR spectra of DUT-5 (black), MIXDUT-5-amine(x) (x=25, green; x=50, blue; x=75, purple) and DUT-5-amine (red).

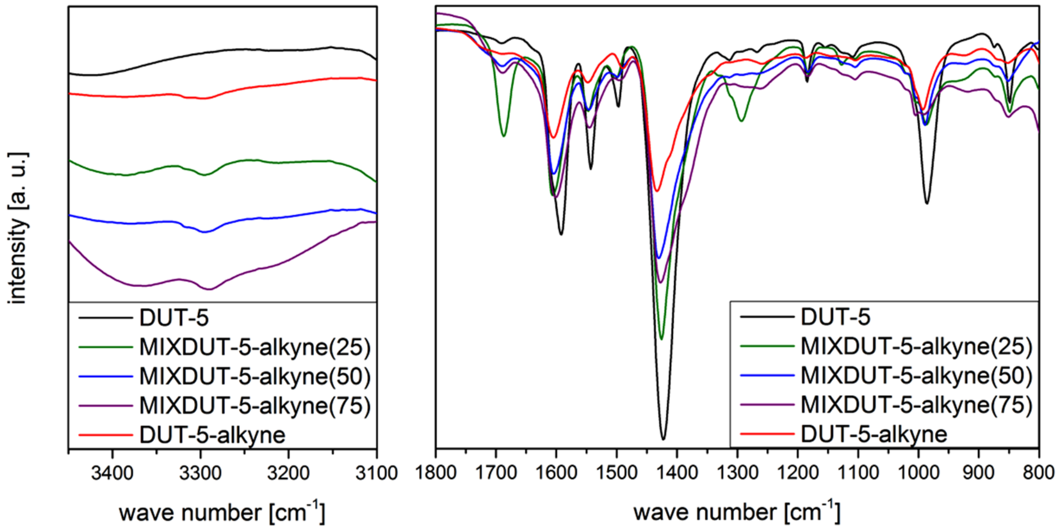


Figure S8: ATR-IR spectra of DUT-5 (black), MIXDUT-5-alkyne(x) (x=25, green; x=50, blue; x=75, purple) and DUT-5-alkyne (red).

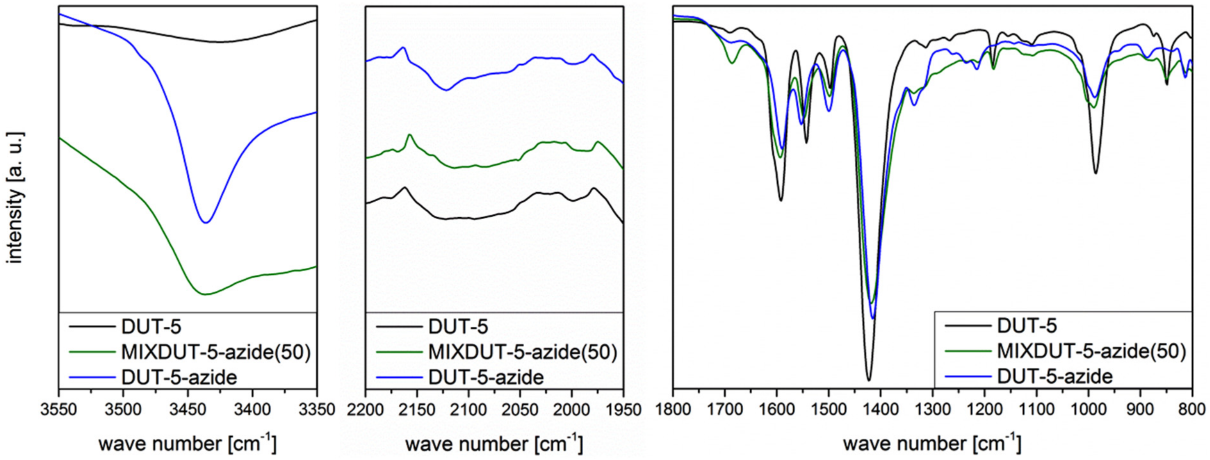


Figure S9: ATR-IR spectra of DUT-5 (black), MIXDUT-5-azide(50) (green) and DUT-5-azide (blue).

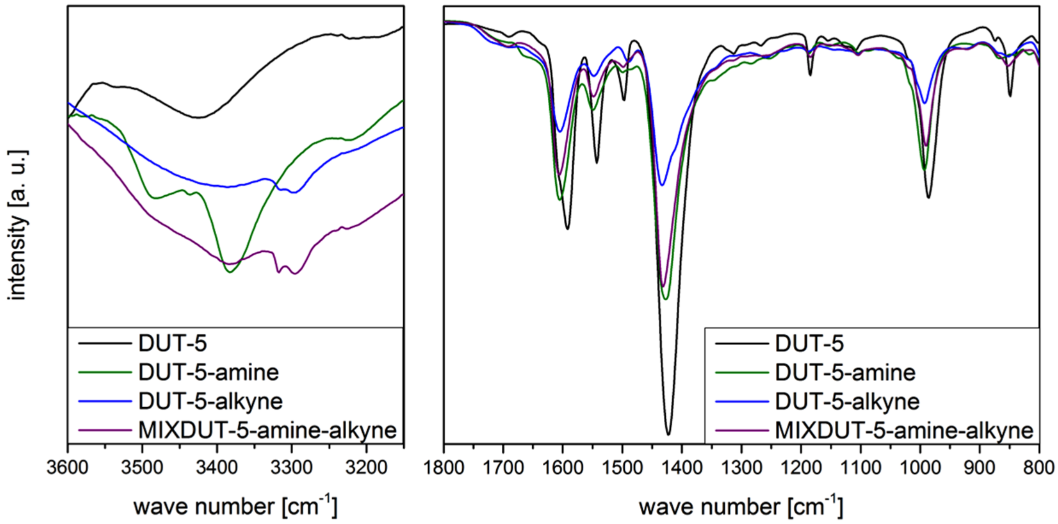


Figure S10: ATR-IR spectra of DUT-5 (black), DUT-5-amine (green), DUT-5-alkyne (blue) and MIXDUT-5-amine(33)alkyne(33) (purple).

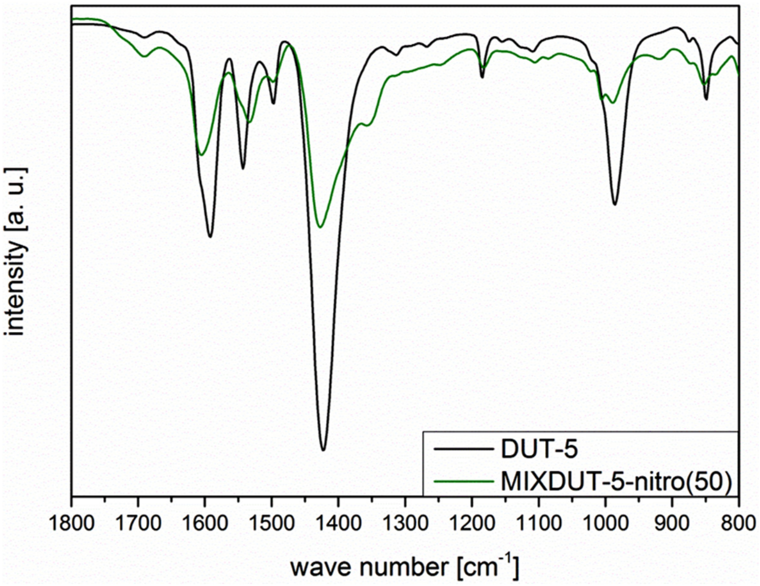


Figure S 11: ATR-IR spectra of DUT-5 (black) and MIXDUT-5-nitro(50) (green).

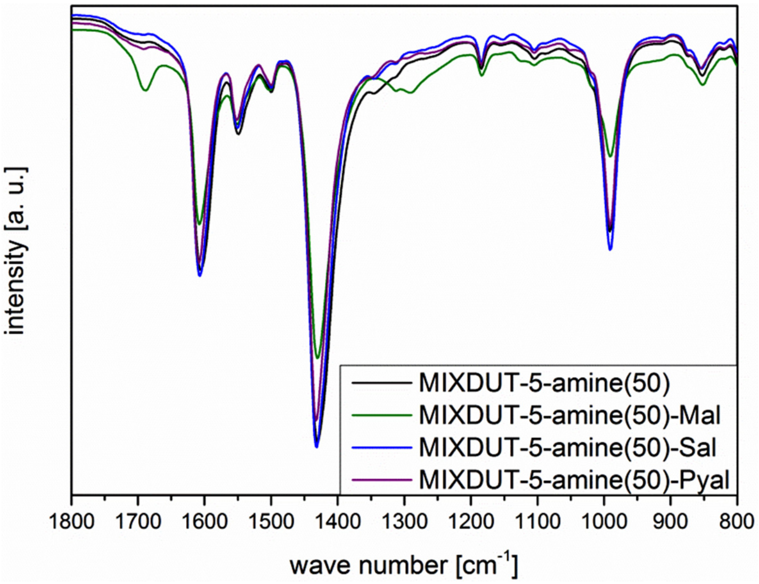


Figure S12: ATR-IR spectra of MIXDUT-5-amine(50) (black) and modified MIXDUT-5-amine(50)-mod (mod=Mal, green; mod=Sal, blue; mod=Pyal, purple).

7. N_2 physisorption measurements

Prior to the nitrogen physisorption the samples were activated for 20 h at 130 °C in vacuum. Measurements were carried out using a Belsorp mini II from BEL Japan. The specific surface area was determined in the range $p/p_0=0.02 – 0.20$ using the BET method and the BEL Master software. The micropore volume was determined using the t-plot method.

Table S5. Specific surface area and micropore volume of functionalized DUT-5 and mixed-linker DUT-5 compared to pure DUT-5.

material	S_{BET} [m²/g]	micropore volume [cm³/g]
DUT-5	1880	0.61
DUT-5-amine	1570	0.58
DUT-5-alkyne	1270	0.40
DUT-5-nitro	550	0.15
DUT-5-azide	540	0.16
MIXDUT-5-amine(25)	1600	0.54
MIXDUT-5-amine(50)	1630	0.58
MIXDUT-5-amine(75)	1630	0.59
MIXDUT-5-alkyne(25)	650	0.17
MIXDUT-5-alkyne(50)	1350	0.42
MIXDUT-5-alkyne(75)	970	0.29
MIXDUT-5-amine(33)-alkyne(33)	1630	0.56
MIXDUT-5-nitro(50)	700	0.22
MIXDUT-5-azide(50)	820	0.25

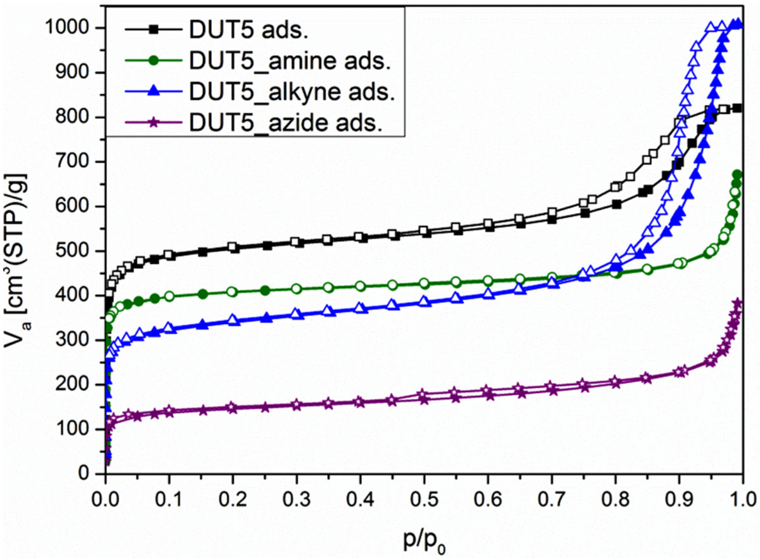


Figure S13. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), DUT-5-amine (green), DUT-5-alkyne (blue) and DUT-5-azide (purple).

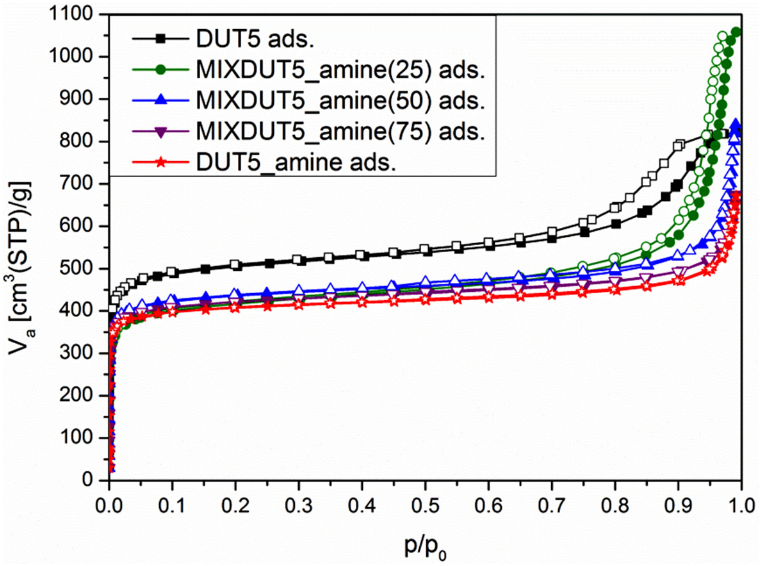


Figure S14. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), MIXDUT-5-amine(x) (x=25, green; x=50, blue; x=75, purple) and DUT-5-amine (red).

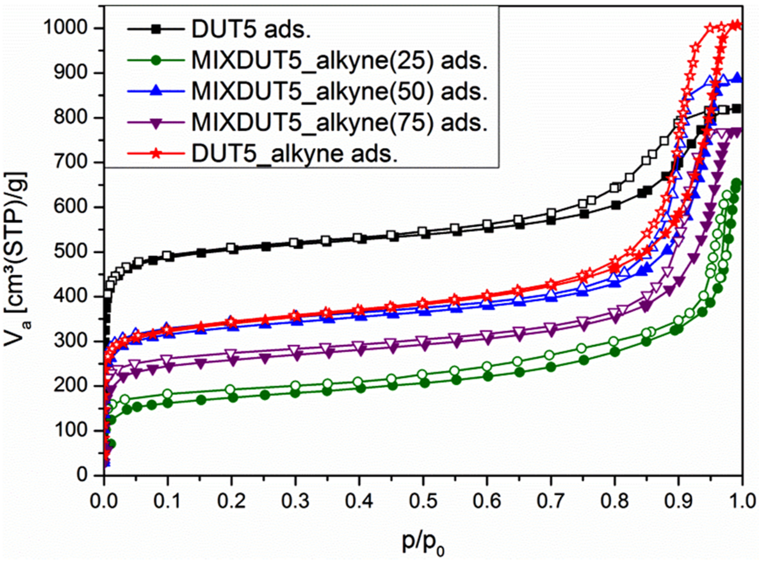


Figure S15. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), MIXDUT-5-alkyne(x) (x=25, green; x=50, blue; x=75, purple) and DUT-5-alkyne (red).

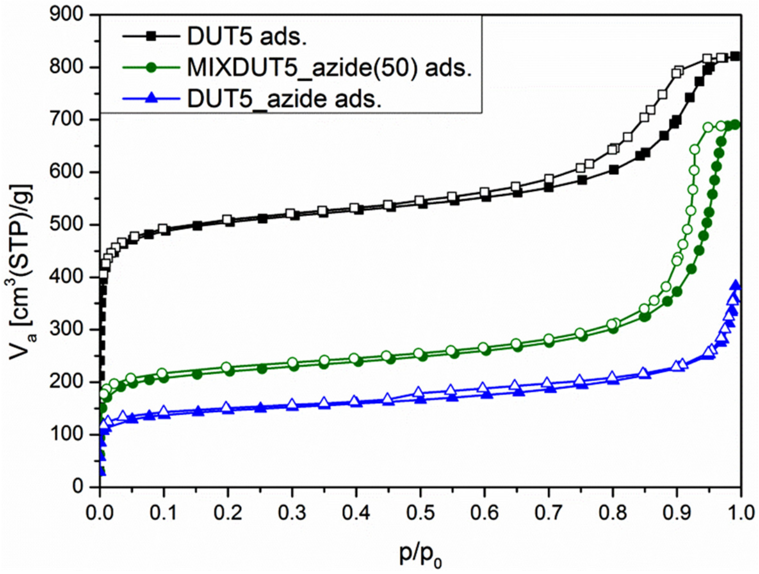


Figure S16. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), MIXDUT-5-azide(50) (green) and DUT-5-azide (blue).

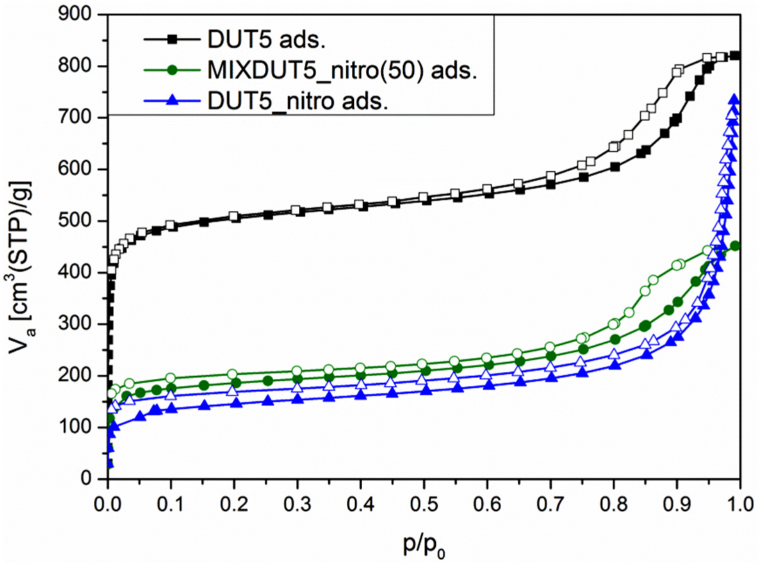


Figure S17: Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), MIXDUT-5-nitro(50) (green) and DUT-5-nitro (blue).

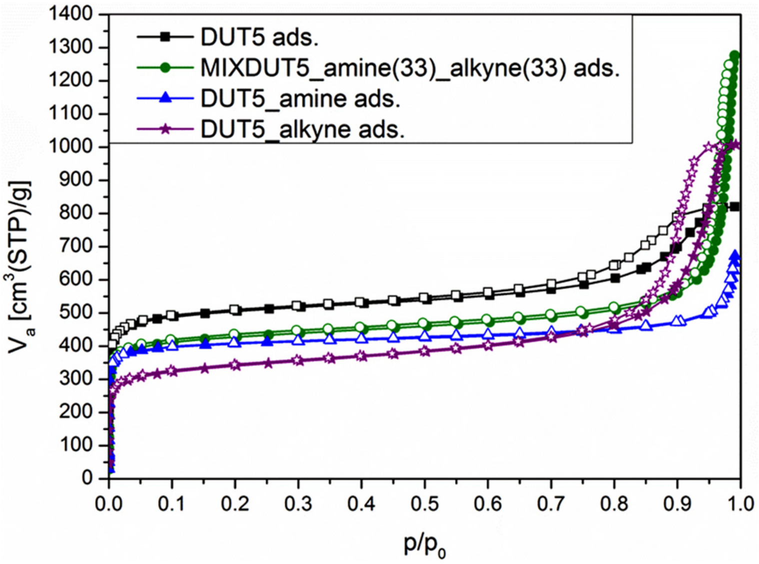


Figure S18. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of DUT-5 (black), MIXDUT-5-amine(33)-alkyne(33) (green), DUT-5-amine (blue) and DUT-5-alkyne (purple).

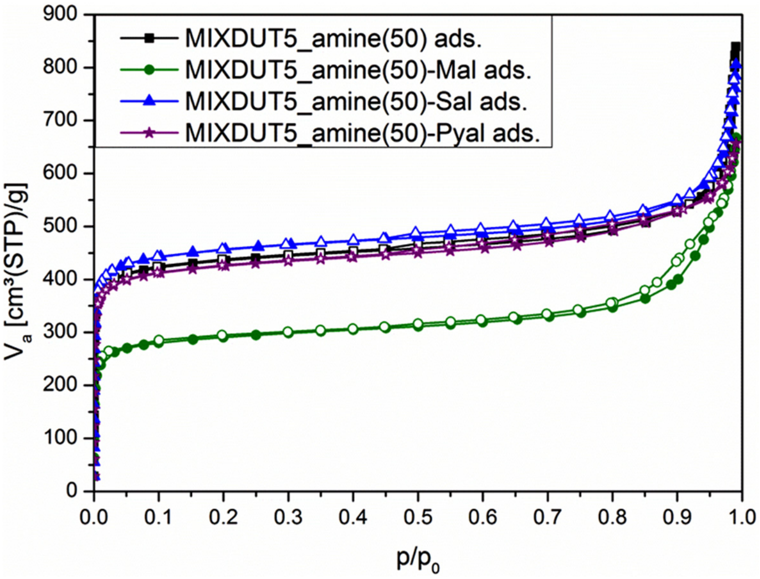


Figure S19. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of MIXDUT-5-amine(50) (black), MIXDUT-5-amine(50)-Mal (green), MIXDUT-5-amine(50)-Sal (blue) and MIXDUT-5-amine(50)-Pyal (purple).

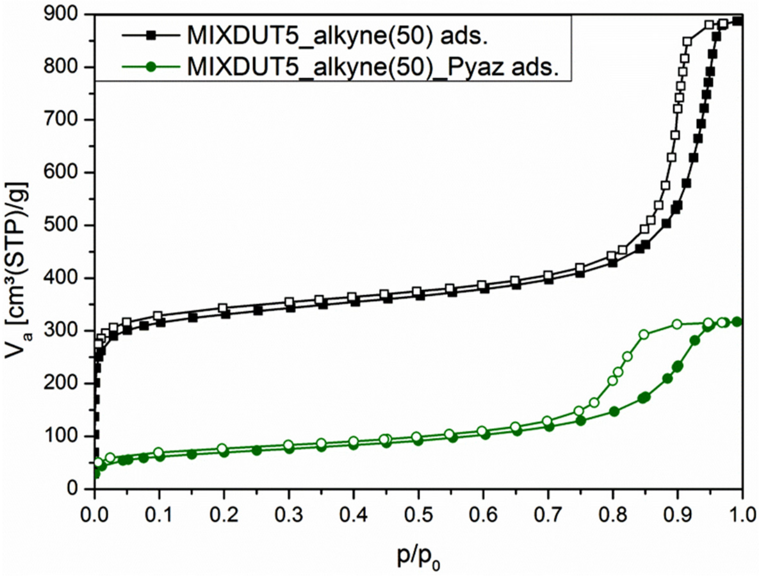


Figure S20. Adsorption (filled symbols) and desorption (hollow symbols) isotherms of MIXDUT-5-alkyne(50) (black) and MIXDUT-5-alkyne(50)-Pyaz (green).

8. Thermogravimetric analysis (TG)

Differential thermal analysis/thermogravimetry (DTA/TG) was performed with a NETZSCH STA 409C applying α-Al_2O_3 as crucible material and reference sample. The samples were heated under air flow from room temperature to 1000 °C with a heating rate of 5 K/min.

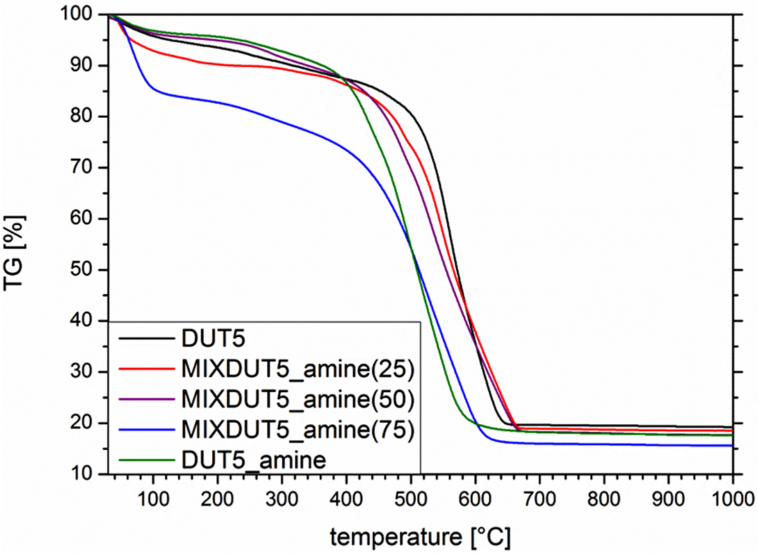


Figure S21. Thermogravimetric analysis of DUT-5 (black), MIXDUT-5-amine(x) (x=25, red; x=50, purple; x=75, blue) and DUT-5-amine (green).

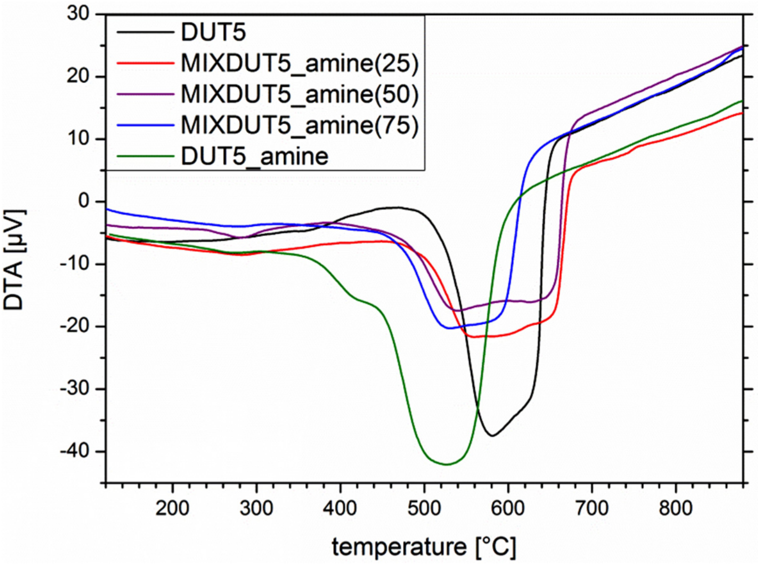


Figure S22. DTA analysis of DUT-5 (black), MIXDUT-5-amine(x) (x=25, red; x=50, purple; x=75, blue) and DUT-5-amine (green).

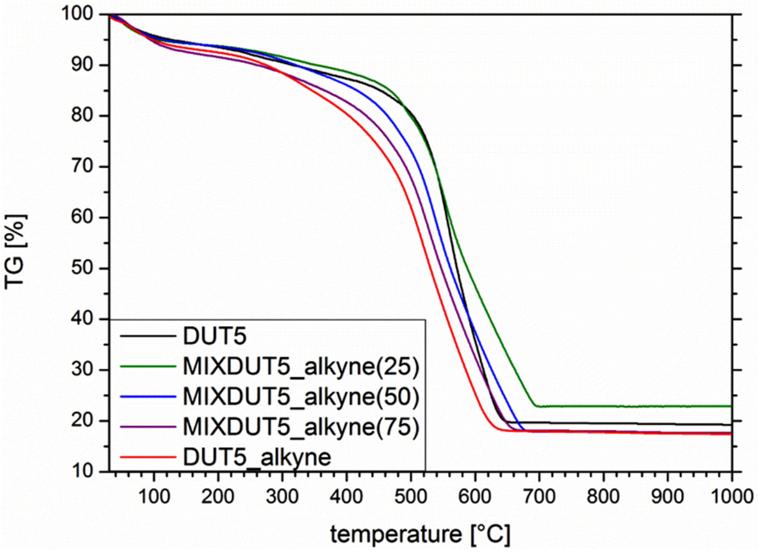


Figure S23. Thermogravimetric analysis of DUT-5 (black), MIXDUT-5-alkyne(50) (green) and DUT-5-alkyne (blue).

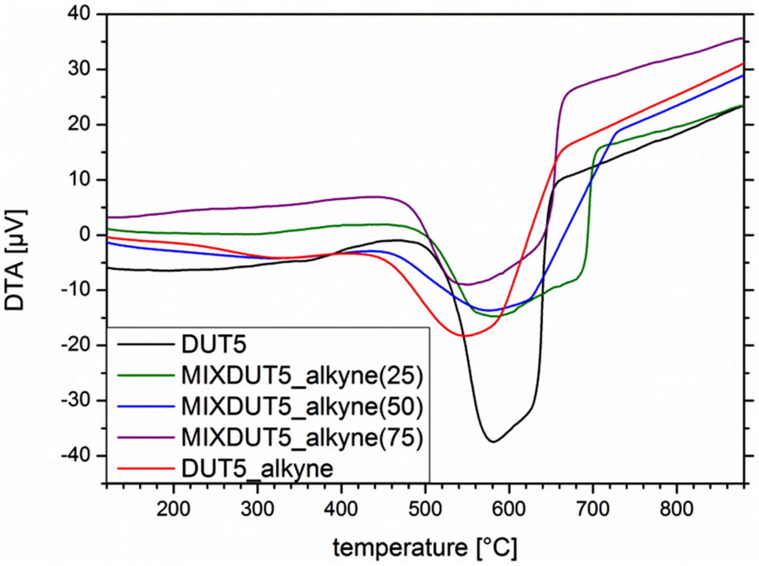


Figure S24. DTA analysis of DUT-5 (black), MIXDUT-5-alkyne(50) (green) and DUT-5-alkyne (blue).

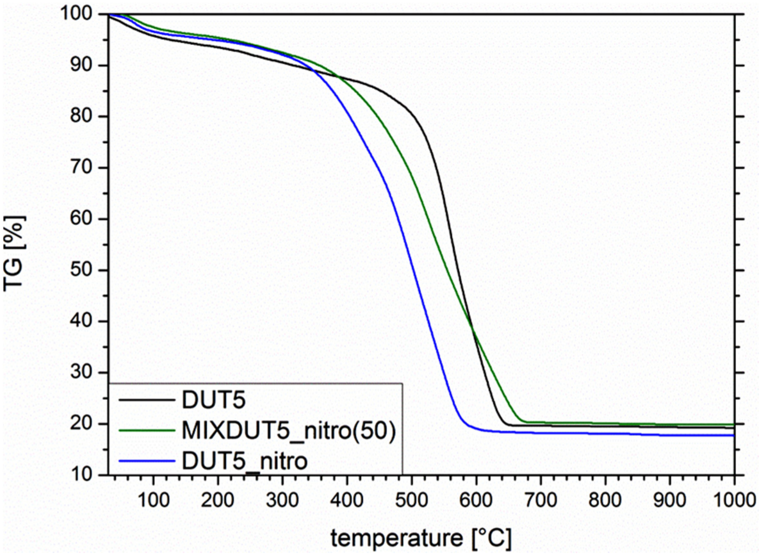


Figure S25. Thermogravimetric analysis of DUT-5 (black), MIXDUT-5-nitro(50) (green) and DUT-5-nitro (blue).

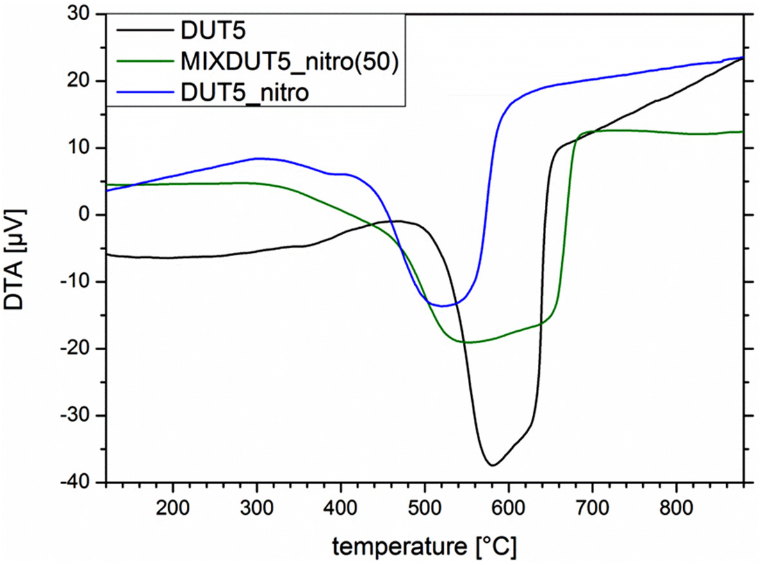


Figure S26. DTA analysis of DUT-5 (black), MIXDUT-5-nitro(50) (green) and DUT-5-nitro (blue).

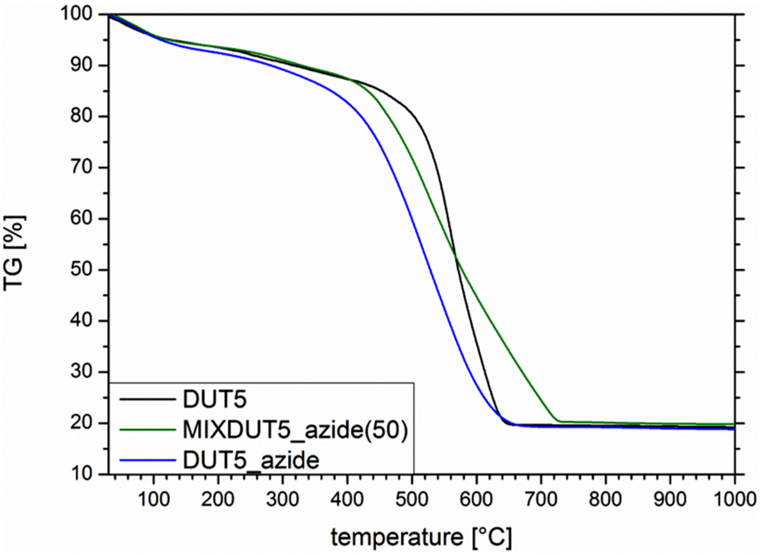


Figure S27. Thermogravimetric analysis of DUT-5 (black), MIXDUT-5-azide(50) (green) and DUT-5-azide (blue).

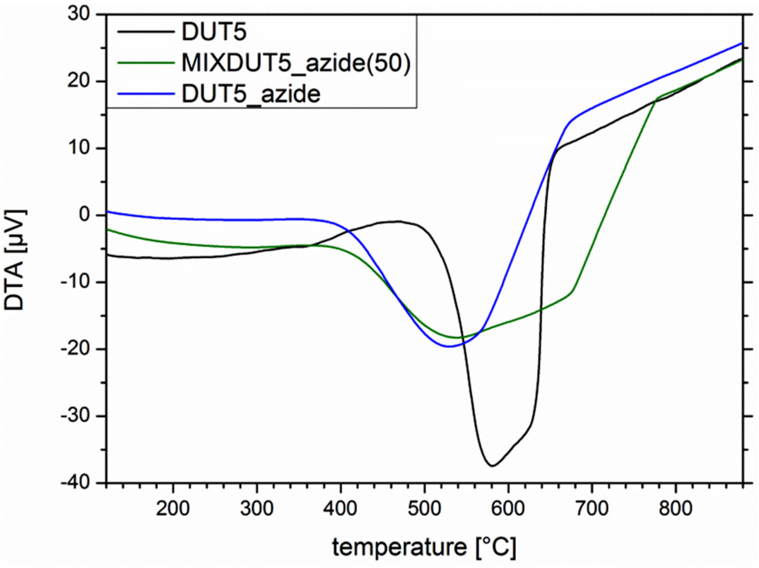


Figure S28. DTA analysis of DUT-5 (black), MIXDUT-5-azide(50) (green) and DUT-5-azide (blue).

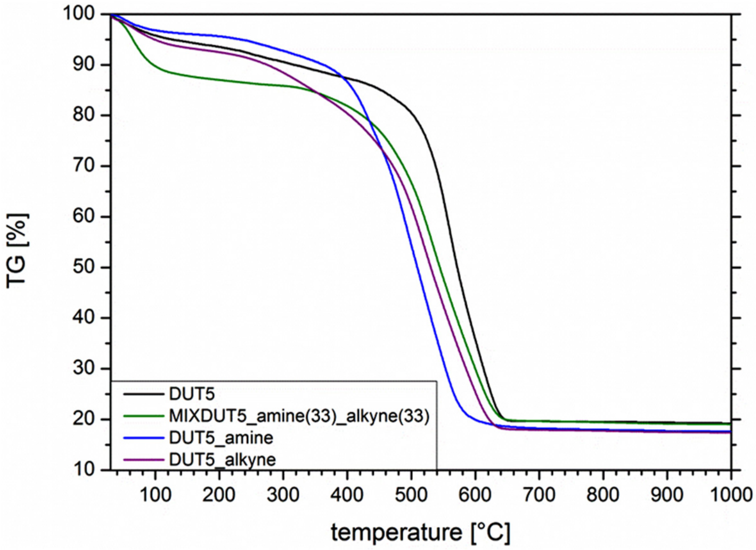


Figure S29. Thermogravimetric analysis of DUT-5 (black), MIXDUT-5-amine(33)-alkyne(33) (green), DUT-5-amine (blue) and DUT-5-alkyne (purple).

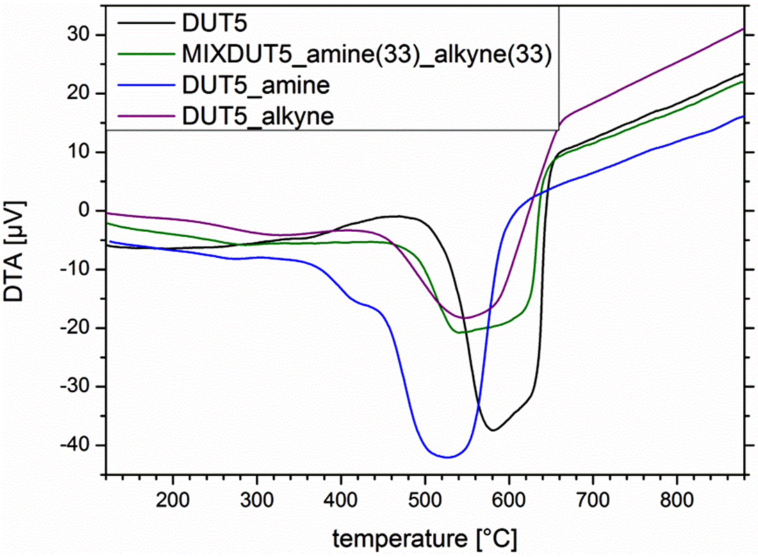


Figure S30. DTA analysis of DUT-5 (black), MIXDUT-5-amine(33)-alkyne(33) (green), DUT-5-amine (blue) and DUT-5-alkyne (purple).

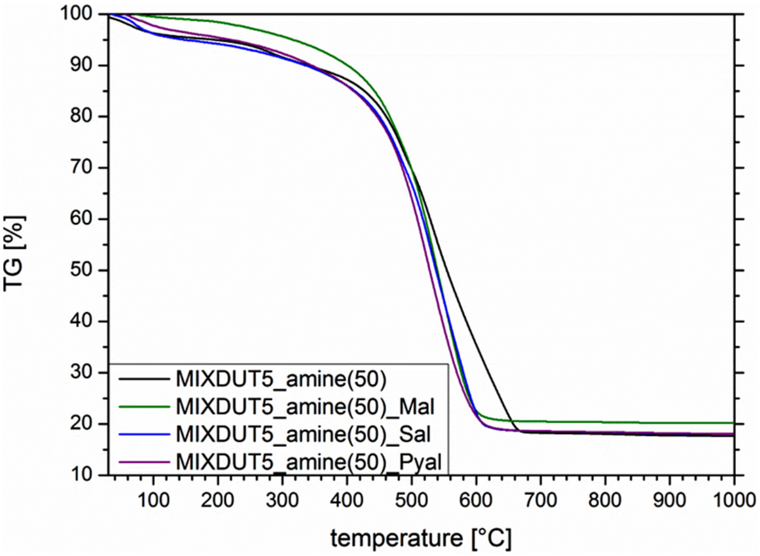


Figure S31. Thermogravimetric analysis of MIXDUT-5-amine(50) (black), MIXDUT-5-amine(50)-Mal (green), MIXDUT-5-amine(50)-Sal (blue) and MIXDUT-5-amine(50)-Pyal (purple).

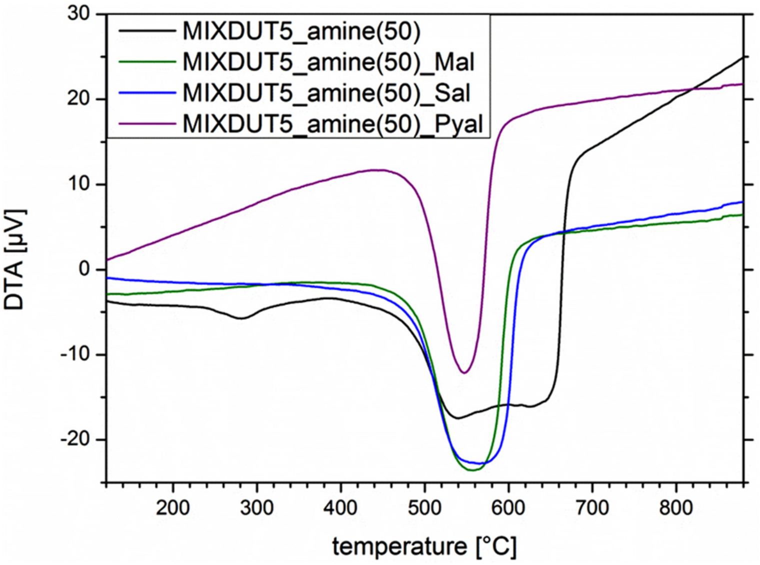


Figure S32. DTA analysis of MIXDUT-5-amine(50) (black), MIXDUT-5-amine(50)-Mal (green), MIXDUT-5-amine(50)-Sal (blue) and MIXDUT-5-amine(50)-Pyal (purple).

9. Thermogravimetric analysis coupled with infrared spectroscopy (TG-IR)

Thermogravimetric Analysis (TGA) coupled with FTIR online gas analysis was performed using a NETZSCH STA 449 F3 connected to a BRUKER TensorII. The Samples were heated in 10 % O_2/He (total gas flow: 50 mL/min) with 5 K/min from 50 °C to 1000 °C. FTIR spectra were recorded during the temperature treatment using a BRUKER gas cell (TGA-IR) and a liquid nitrogen cooled MCT detector. Transfer line and gas cell were heated to 230 °C. FTIR data was evaluated focusing on NO_2 and CO_2 formation to derive a measure for the total nitrogen content of each sample by integration of characteristic spectral features.

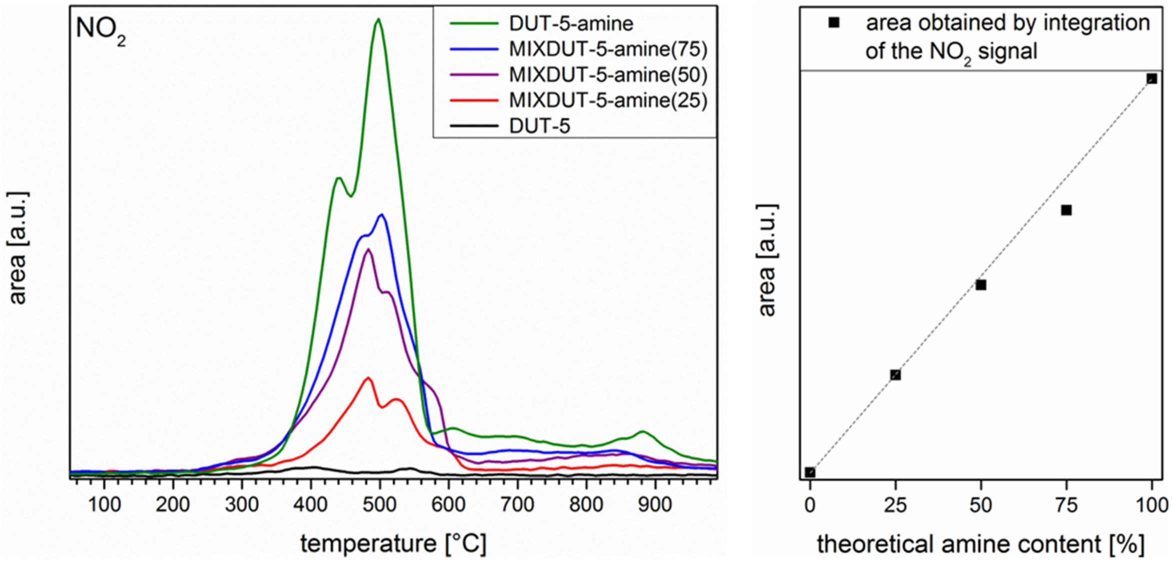


Figure S33: Left: Integration of the NO_2-band in the IR spectra of DUT-5 (black), MIXDUT-5-amine(x) (x=25, red; x=50, purple; x=75, blue) and DUT-5-amine (green) over the whole temperature range; right: comparison of the measured NO_2-area and the theoretical amine content.

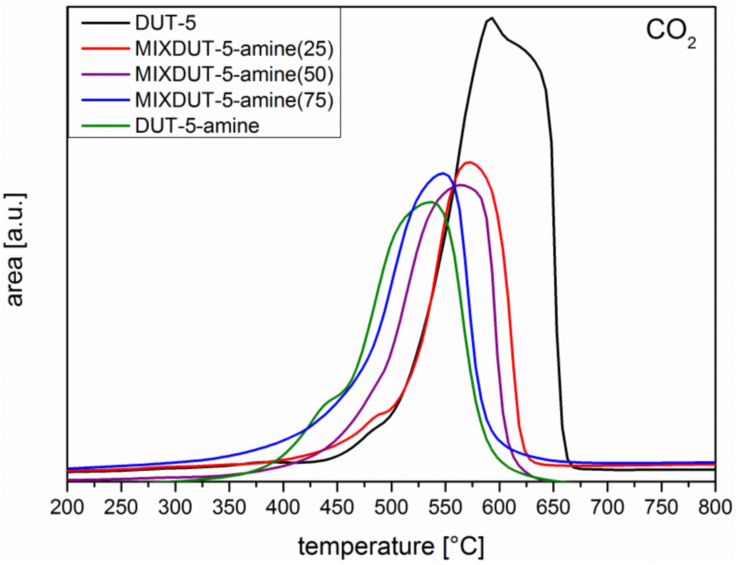


Figure S34: Integration of the CO_2-band in the IR spectra of DUT-5 (black), MIXDUT-5-amine(x) (x=25, red; x=50, purple; x=75, blue) and DUT-5-amine (green) over the whole temperature range.

10. Nuclear magnetic resonance (NMR) spectroscopy

6 mg of the samples were digested in 0.5 mL NaOH/D_2O. Spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to tetramethylsilane.

Literature

[1] V. K. Olkhovik, D. A. Vasilevskii, A. A. Pap, G. V. Kalechyts, Y. V. Matveienko, A. G. Baran, N. A. Halinouski, V. G. Petushok, *ARKIVOC* **2008**, 69-93.

[2] P. V. Dau, S. M. Cohen, *CrystEngComm* **2013**, *15*, 9304-9307.

[3] R. K. Deshpande, J. L. Minnaar, S. G. Telfer, *Angew. Chem. Int. Ed.* **2010**, *49*, 4598-4602.

[4] K. Leus, M. Vandichel, Y.-Y. Liu, I. Muylaert, J. Musschoot, S. Pyl, H. Vrielinck, F. Callens, G. B. Marin, C. Detavernier, P. V. Wiper, Y. Z. Khimyak, M. Waroquier, V. Van Speybroeck, P. Van der Voort, *J. Catal.* **2012**, *285*, 196-207.