Supporting Information

A series of sulfonic acid functionalized mixed-linker DUT-4 analogues: synthesis, gas sorption properties and catalytic performance

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Table S1. Detailed amounts of the starting compounds for the synthesis of the mixed-linker MOFs and the experimentally obtained linker ratios determined by means of ¹H NMR. The Langmuir surface area and pore volume of the resulting DUT-4-SO₃H(x)

	Synthesis						Structural Properties		
Sample	Al(NO₃)₃ mmol	Theoretical ratio	NDC (mmol)	NDC-2SO₃H (mmol)	DMF (mL)	Experimentally obtained ratio (determined by ¹ H NMR)	S _{Langmuir} (m²/g)	S _{BET} (m²/g)	V _{mic} (cm³/g)
DUT-4	0.69	100/0	0.6	0	15	100/0	1955	1650	0.63
DUT-4-SO ₃ H(10)	0.69	90/10	0.54	0.06	15	95.3/4.7	1807	1524	0.58
DUT-4-SO ₃ H(20)	0.69	80/20	0.48	0.12	15	88.2/11.8	1650	1457	0.51
DUT-4-SO ₃ H(30)	0.69	70/30	0.42	0.18	15	75/25	1450	1135	0.47
DUT-4-SO ₃ H(40)	0.69	60/40	0.36	0.24	15	69.4/30.6	975	580	0.28
DUT-4-SO ₃ H(50)	0.69	50/50	0.3	0.3	15	54.4/45.6	820	546	0.23

The reaction temperature and time for all the studied materials were performed at 150 $^{\circ}$ C with a heating rate of 2 $^{\circ}$ C/min for 24 h.



Figure S1. XRPD patterns of the sulfonic acid functionalized DUT-4 analogues with 2 theta angle range from 5 to 10.



Figure S2. FT-IR spectra of the sulfonic acid functionalized mixed-linker DUT-4 analogues (left) and FT-IR spectra in the range of 800 -1800 cm⁻¹ (right).



Figure S3. Isosteric heat of CO_2 adsorption (Q_{st}) for the series of DUT-4-SO₃H(x) materials

The isosteric heat of CO_2 adsorption (Q_{st}) was calculated from the obtained CO_2 adsorption isotherms at different temperatures by employing the Clausius-Clapeyron equation:

$$Q_{st} = -R[\frac{\partial(\ln P)}{\partial(1/T)}]_n$$

Where P is the pressure, n is the amount of adsorbed CO_2 , T is temperature, R is the universal gas constant. We plotted InP versus 1/T for different temperatures and the slope of these lines was used to determine the isosteric heat of adsorption at each pressure point.



Figure S4. High pressure CO₂ adsorption (solid symbols) and desorption (open symbols) isotherms of all the obtained materials measured at 273 K (left) and 303 K (right), respectively.

Table S2: Overview of the optimized unit cell parameters at the experimental volume of 2064 Å³. The angle ω represents the pore opening angle. Hence a decrease of this angle indicates a contraction of the pore.

Structure	a [Å]	b [Å]	c [Å]	α [deg]	β [deg]	γ [deg]	ω [deg]
DUT-4	20.90	6.65	14.85	90.0	90.0	90.0	70.8
DUT-4-SO₃H(25)	21.07	6.70	14.63	90.3	89.9	90.0	69.5
DUT-4-SO₃H(100)	21.05	6.73	14.58	90.0	90.7	90.0	69.4

Table S3: Overview of the calculated pore and textural properties. The three different types of pore diameters are defined as (1) D_i : the largest included sphere; (2) D_f : the largest free sphere; (3) D_{if} : the largest included sphere along the free sphere path. The accessible volume (AV), accessible surface area (ASA) and void fraction decrease significantly within the series. All properties are calculated for a structure optimized at the experimental unit cell volume of 2064 Å³.

	Pore diameters			Textural properties				
Structure	Di	Df	D _{if}	Density	ASA	AV	Void fraction	
	[Å]	[Å]	[Å]	[g/cm ³]	[m²/g]	[cm ³ /g]	[%]	
DUT-4	8.35	7.96	8.34	0.83	3068	0.42	35.0	
DUT-4-SO₃H(25)	6.93	6.13	6.79	0.96	2736	0.29	27.8	
DUT-4-SO₃H(100)	4.58	3.99	4.58	1.35	1879	0.09	12.8	



Figure S5: Reactant and product structures of the catalytic reaction optimized on the B3LYP/6-311+G(d,p) level of theory using a SCRF continuum solvent model to mimic the catalytic environment.