Supporting Information

Linker Functionalization Triggers an Alternative 3D-Topology for Zn-Isophthalate-4,4'-Bipyridine Frameworks

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S1 Linker Synthesis

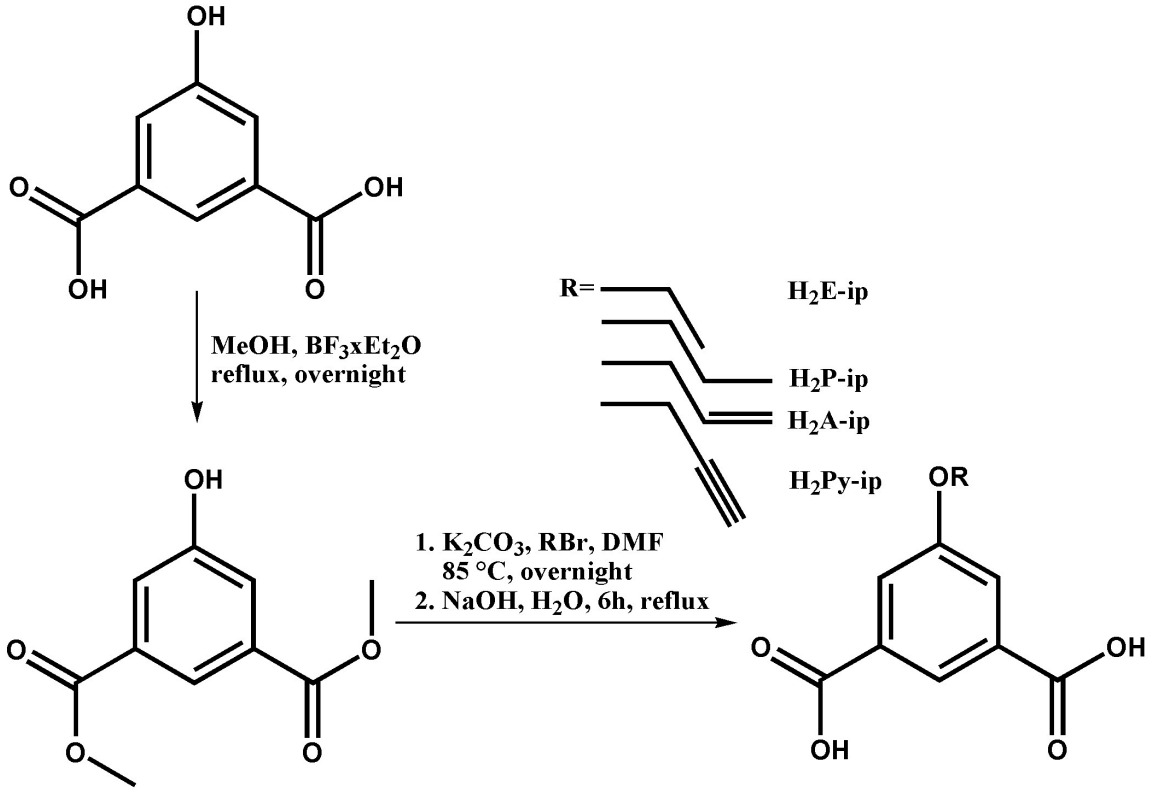

Figure S1:Synthetic route towards functionalized isophthalic acid linker molecules.

Table S1: Amount of bromohydrocarbons used for the linker synthesis.

Bromohydrocarbon	Mass [g]	Volume [ml]
Bromoethane	3.11	2.11
1-Bromopropane	3.48	2.86
Allylbromid	3.42	2.45
3-Bromoprop-1-yne	3.36	2.16

Table S2: Linker yields.

Linker	Theo. Yield [g]	Pract. Yield [g]	Yield [%]
5-Ethoxyisophthalic acid	2.0	0.58	29.00
5-Propoxyisophthalic acid	2.13	0.86	40.38
5-(Allyloxy)isophthalic acid	2.11	1.57	74.41
5-(Prop-2-ynyloxy)isophthalic acid	2.1	1.4	66.66

S2 PXRD Patterns and Cell Parameter Fittings

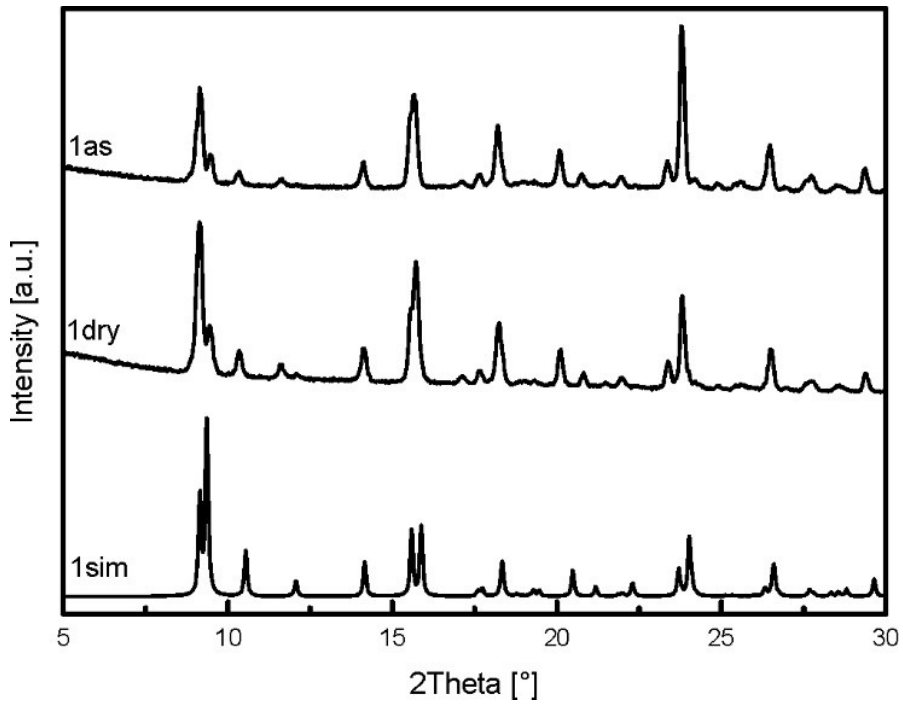

Figure S2: PXRD patterns of compound **1** in the as-synthesized (as) and activated state (dry) compared to the pattern calculated from the single crystal structure (sim).

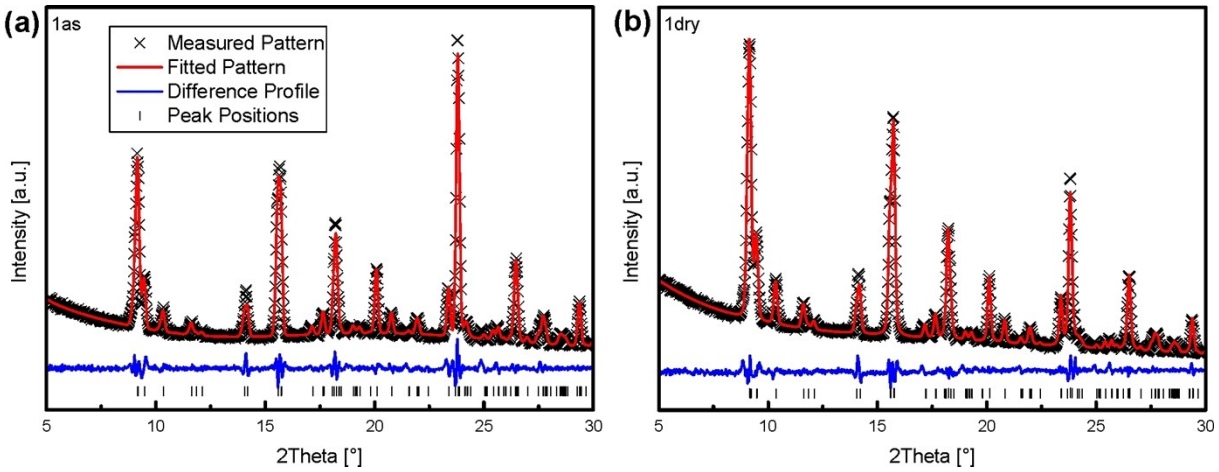

Figure S3: Pawley fits to the PXRD patterns of compounds **1as** (a) and **1dry** (b). The measured patterns are shown as black crosses, the fitted patterns as red lines, the difference plots as blue lines and the theoretical peak positions are marked by black tick marks.

Table S3: Summary of the unit cell parameters calculated by the Pawley method PXRD patterns (**1as** and **1dry**), compared to the cell parameters derived from the single crystal X-ray diffraction (**1scxrd**).

Compound	1as	1dry	1scxrd
a / Å	10.1021(16)	10.0930(18)	10.0944(3)
b / Å	10.412(2)	10.4174(15)	10.3898(2)
c / Å	10.7426(18)	10.7606(17)	10.4930(3)
α / °	64.944(7)	64.878(7)	65.925(2)
β / °	75.357(9)	75.409(10)	75.649(2)
γ / °	75.795(10)	75.868(10)	76.069(2)
V / Å^3	977.97(3)	979.1(3)	961.20(5)
Space Group	*P*-1	*P*-1	*P*-1
R_{wp}	4.96%	5.27%	
R_{exp}	2.32%	2.55%	

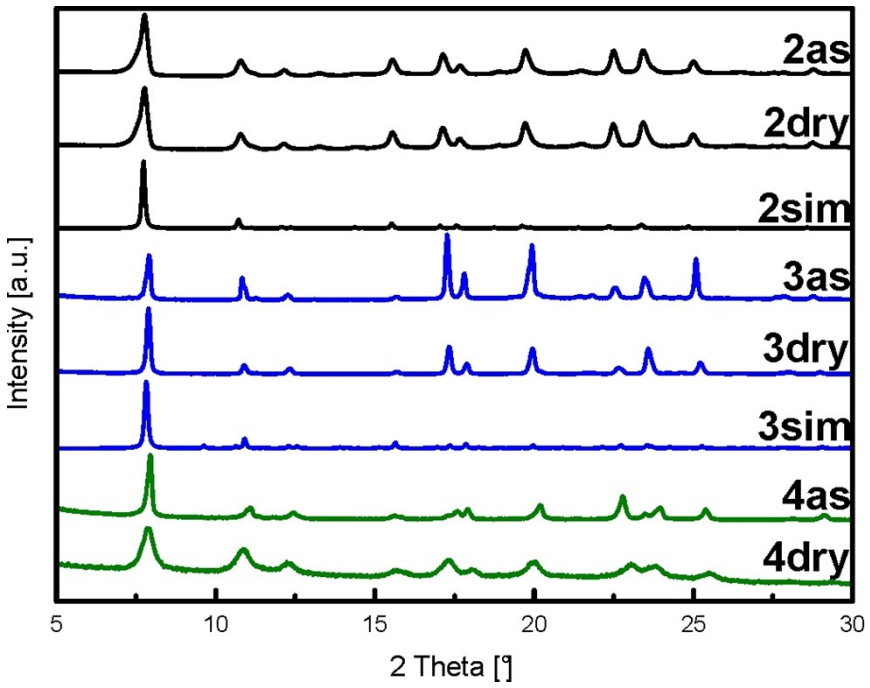

Figure S4: PXRD patterns of materials **2** (black), **3** (blue) and **4** (green).

Table S4: Summary of the cell parameters for the as-synthesized (as) and activated (dry) materials determined by Pawley refinement of the PXRD patterns, as well as the unit cell parameters obtained from SCXRD (scxrd).

	2as	2dry	2scxrd	3as	3dry	3scxrd	4as	4dry
a / Å	16.3535(11)	16.3616(11)	16.4960(7)	11.3989(18)	11.416(2)	11.3963(4)	15.959(3)	15.912(7)
b / Å	15.7639(11)	15.7700(12)	15.8918(6)	15.792(3)	15.738(2)	15.6396(6)	15.5879(11)	15.56(3)
c / Å	11.307(5)	11.310(5)	11.4039(4)	16.466(3)	16.426(3)	16.3032(6)	11.083(4)	10.8640(13)
α / °	90	90	90	90	90	90	90	90
β / °	90	90	90	95.557(9)	95.30(3)	96.459	90	90
γ / °	90	90	90	90	90	90	90	90
V / Å^3	2914.8(14)	2918.319(13)	2989.5(2)	2951.1(9)	2938.6(10)		2757.1(11)	2689(5)
Space Group	*Pbam*	*Pbam*	*Pbam*	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Pbam*	*Pbam*
R_{wp}	3.19%	3.30%		9.30%	8.51%		9.53%	6.25%
R_{exp}	0.59%	1.03%		2.55%	2.68%		4.22%	1.65%

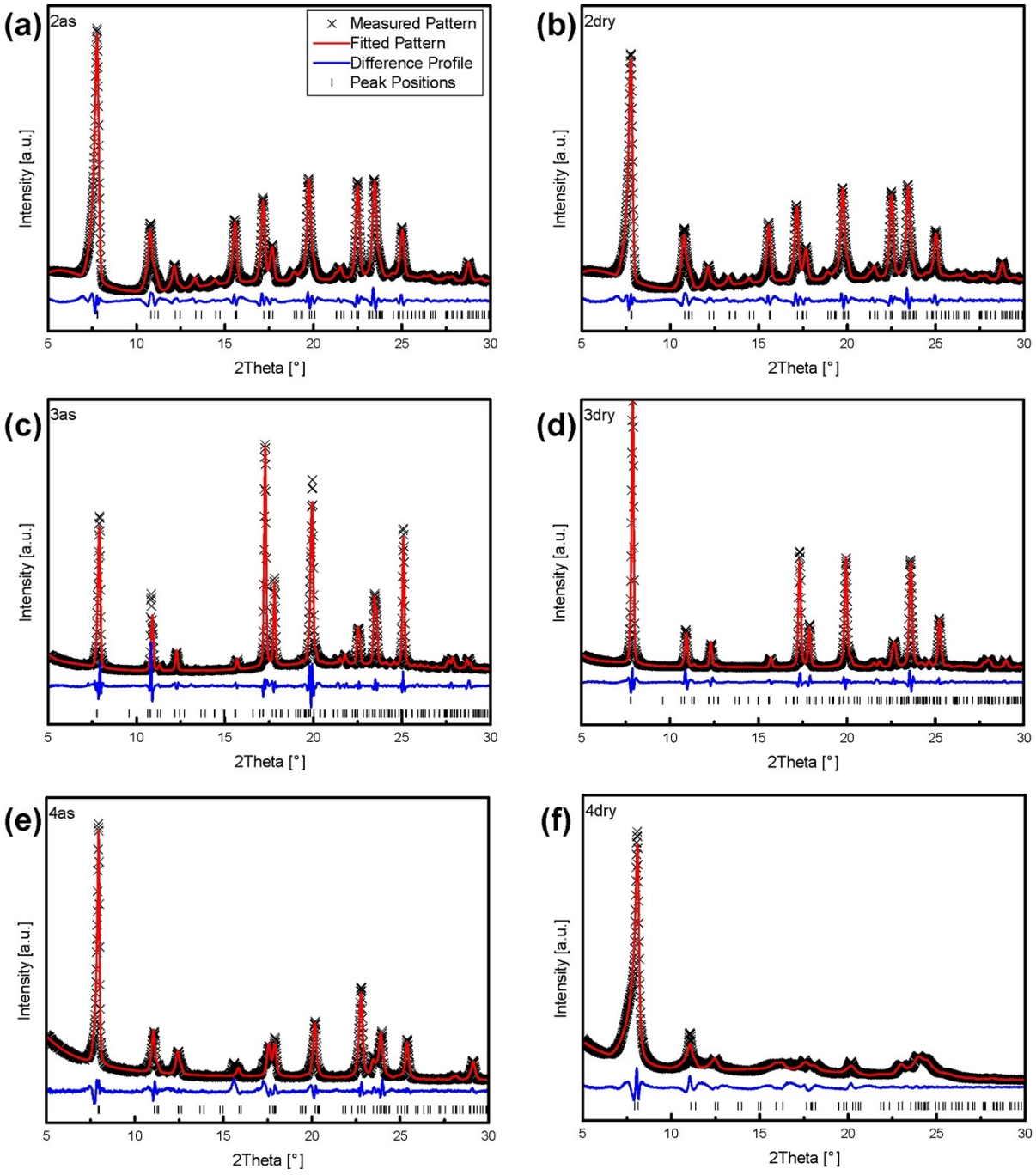

Figure S5: Pawley fits to the PXRD patterns of compounds **2as** (a), **2dry** (b), **3as** (c), **3dry** (d), **4as** (e) and **4dry** (f). The measured patterns are shown as black crosses, the fitted patterns as red lines, the difference plots asblue lines and the theoretical peak positions are marked by black tick marks.

S3 NMR Data

For the prepared linker molecules H_2E-ip, H_2P-ip, H_2A-ip and H_2Py-ip the following peak positions and integrals were reported from the NMR measurements:

^{1}H NMR of 5-Ethoxyisophthalic acid (200 MHz, DMSO-d_6) δ 8.04 (s, 1H), 7.56 (s, 2H), 4.11 (m, 2H), 1.32 (t, 3H).

^{1}H NMR of 5-Propoxyisophthalic acid (200 MHz, DMSO-d_6) δ 8.06 (s, 1H), 7.63 (s, 2H), 4.03 (t, 2H), 1.75 (q, 2H), 0.99 (t, 3H).

^{1}H NMR of 5-(Allyloxy)isophthalic acid (200 MHz, DMSO-d_6) 7.97 (s, 1H), 7.57 (s, 2H), 5.95 (m, 1H), 5.35 (d, 1H), 5.23 (d, 1H), 4.60 (d, 2H).

^{1}H NMR of 5-(Prop-2-ynyloxy)isophthalic acid (200 MHz, DMSO-d_6) δ 8.11 (s, 1H), 7.72 (s, 2H), 4.95 (d, 2H), 3.64 (s, 1H).

It was not possible to fully remove the DMF from compound **1** even after several attempts using different conditions. Presence of two peaks in the bipy range is due to partial protonation of the bipyridines.

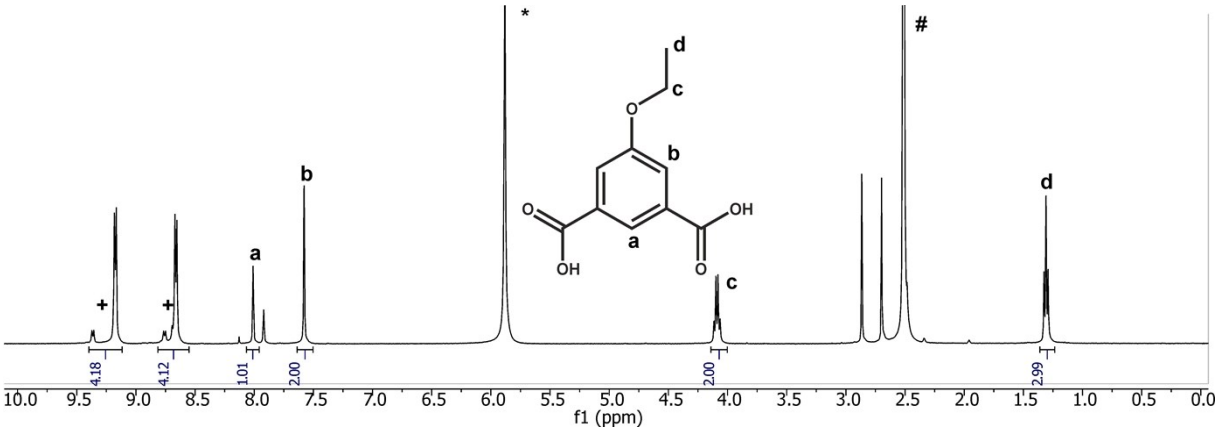

Figure S6: ^{1}H NMR spectrum of **1** (Zn(E-ip)(bipy)) after digestion in DMSO/DCl/D_2O. The signal marked with an asterisk belongs to D_2O/DCl and the DMSO signal is marked with a hash. The crosses mark the bipy signals.

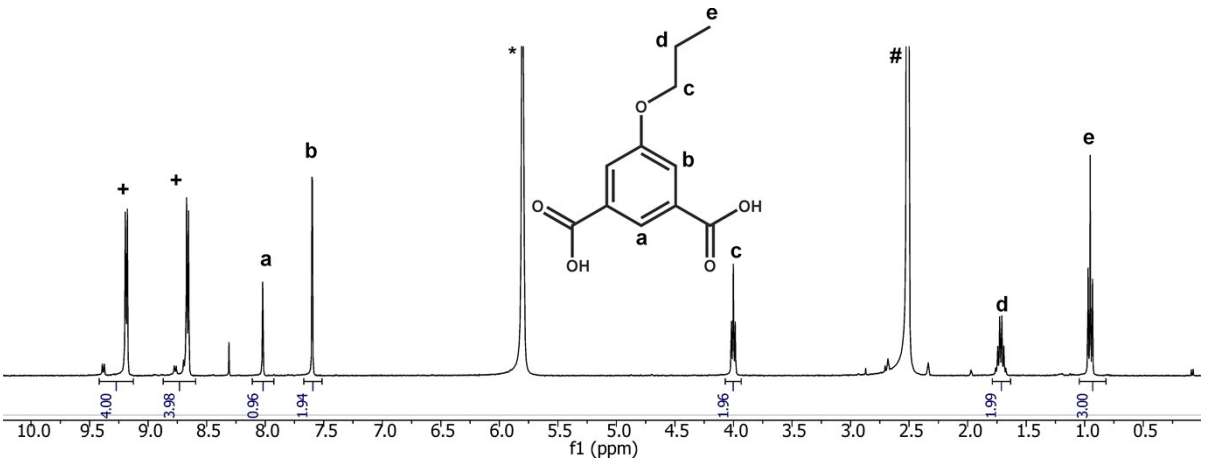

Figure S7: ^{1}H NMR spectrum of **2** (Zn(P-ip)(bipy)) after digestion in DMSO/DCl/D_2O. The signal marked with an asterisk belongs to D_2O/DCl and the DMSO signal is marked with a hash. The crosses mark the bipy signals.

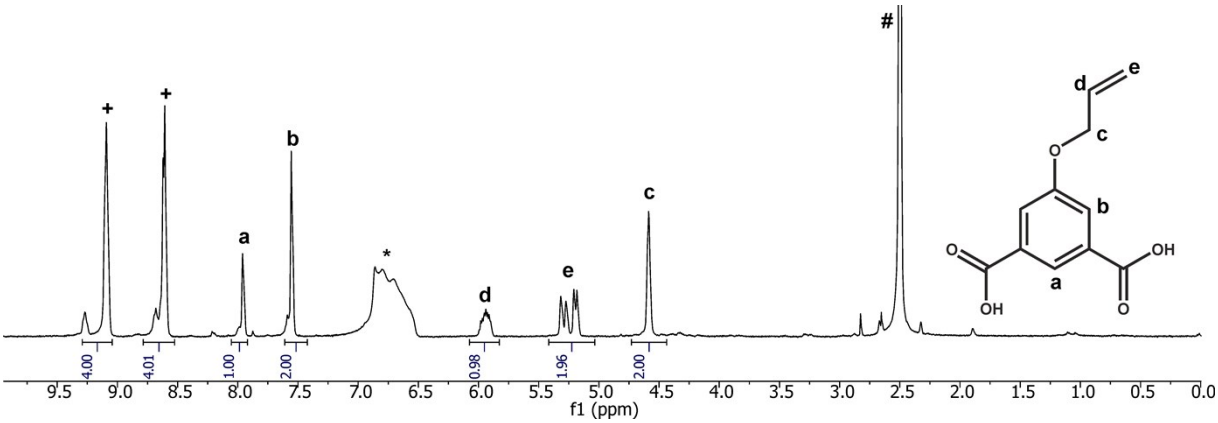

Figure S8: ^{1}H NMR spectrum of **3** (Zn(A-ip)(bipy)) after digestion in DMSO/DCl/D_2O. The signal marked with an asterisk belongs to D_2O/DCl and the DMSO signal is marked with a hash. The crosses mark the bipy signals.

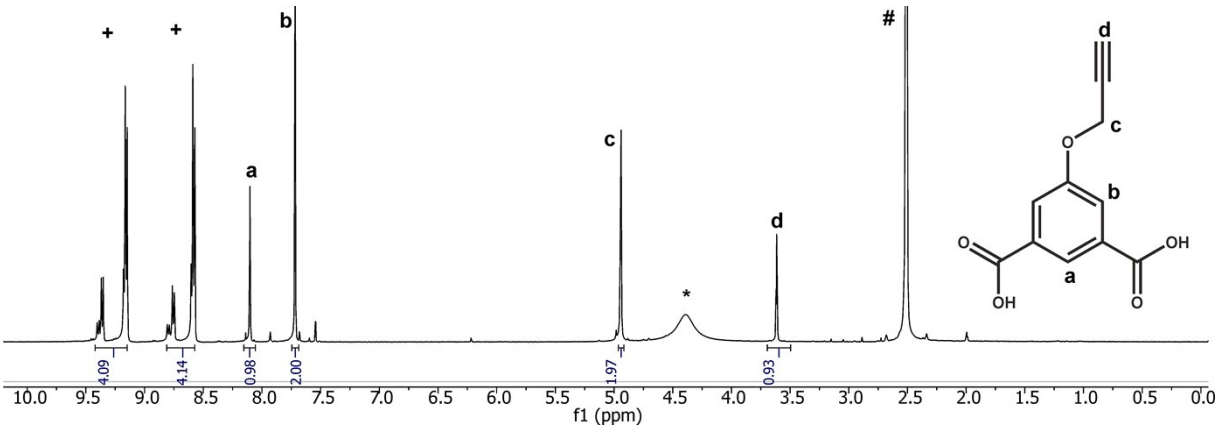

Figure S9: ^{1}H NMR spectrum of **4** (Zn(Py-ip)(bipy)) after digestion in DMSO/DCl/D_2O. The signal marked with an asterisk belongs to D_2O/DCl and the DMSO signal is marked with a hash. The crosses mark the bipy signals.

^{1}H NMR of **(1)** (200 MHz, DCl/D_2O/DMSO-d_6) δ 9.17 (d, 4H), 8.68 (d, 4H), 8.01 (s, 1H), 7.58 (s, 2H), 4.11 (m, 2H), 1.30 (t, 3H).

^{1}H NMR of **(2)** (200 MHz, DCl/D_2O/DMSO-d_6) δ 9.18 (d, 4H), 8.67 (d, 4H), 8.03 (s, 1H), 7.60 (s, 2H), 4.01 (t, 2H), 1.74 (m, 2H), 0.96 (t, 3H).

^{1}H NMR of **(3)** (200 MHz, DCl/D_2O/DMSO-d_6) δ 9.12 (d, 4H), 8.65 (d, 4H), 7.97 (s, 1H), 7.57 (s, 2H), 5.95 (m, 1H), 5.35 (d, 1H), 5.23 (d, 1H), 4.60 (d, 3H).

^{1}H NMR of **(4)** (200 MHz, DCl/D_2O/DMSO-d_6) δ 9.10 (d, 4H), 8.64 (d, 4H), 8.00 (s, 1H), 7.62 (s, 1H), 4.84 (s, 2H), 3.52 (s, 1H).

S4 Infrared Spectroscopy

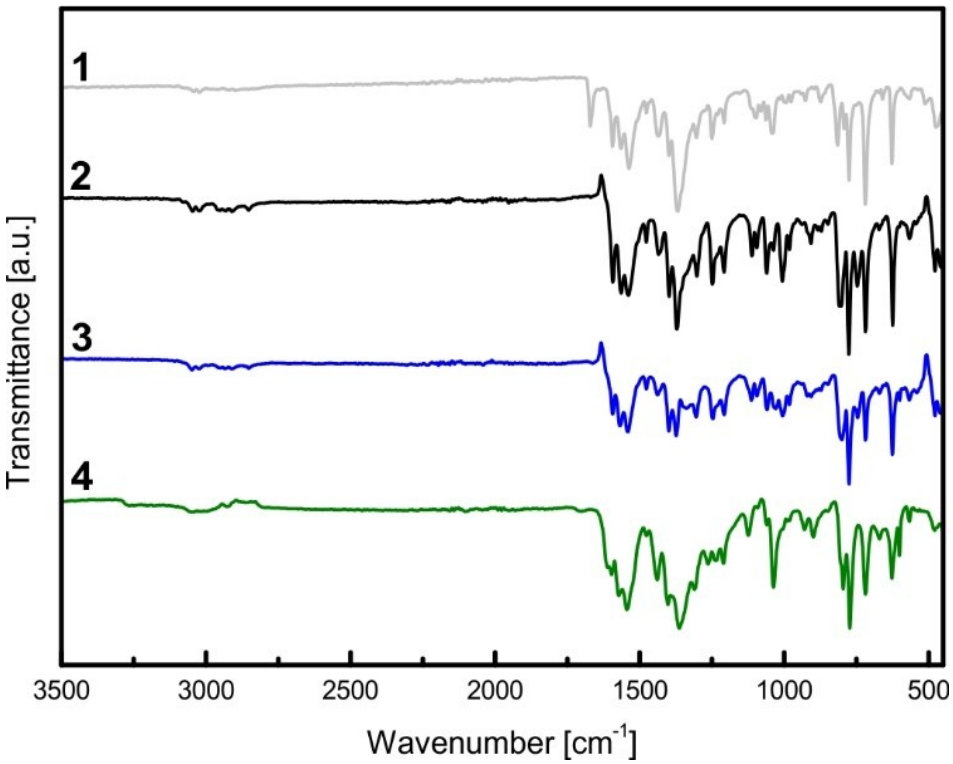

Figure S10: IR spectra of the dried, activated materials **1**, **2**, **3** and **4**. In the spectrum of compound **1** the presence of DMF is clearly visible (strong ν(CO) of the carbonyl group at 1671 cm^{-1}).

S5 Thermogravimetric Analysis

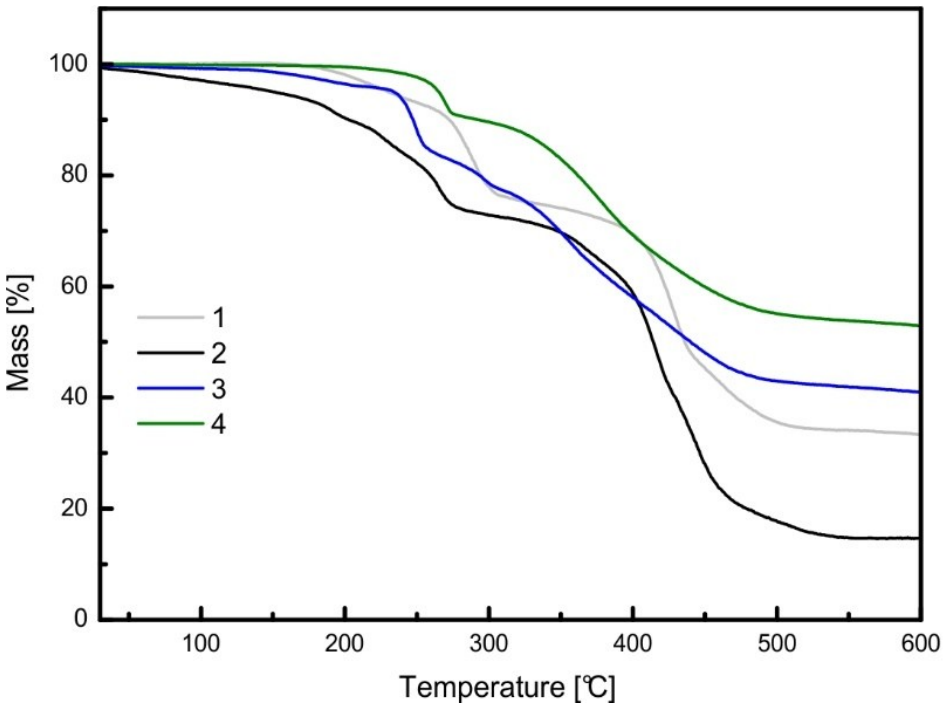

Figure S11: TG curves of compounds **1**, **2**, **3** and **4**. The weight loss of compound **1** starts at relatively high temperatures, suggesting that the DMF hosted in the isolated pores of **1** is trapped.

S6 Single Crystal Diffraction

Identification Code	Compound 1
Empirical formula	$C_{20}H_{16}N_2O_5Zn$
Formula weight	429.72
Temperature/K	111(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.0944(3)
b/Å	10.3898(2)
c/Å	10.4930(3)
α/°	65.925(2)
β/°	75.649(2)
γ/°	76.069(2)
Volume/Å³	961.20(5)
Z	2
ρ_{calc}g/cm³	1.485
μ/mm⁻¹	2.073
F(000)	440
Crystal size/mm³	0.1109 × 0.0734 × 0.0619
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.158 to 152.574
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 13$, $-13 \le l \le 13$
Reflections collected	23586
Independent reflections	3974 [R_{int} = 0.0250, R_{sigma} = 0.0141]
Data/restraints/parameters	3974/18/295
Goodness-of-fit on F²	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0233, wR2 = 0.0606
Final R indexes [all data]	R1 = 0.0250, wR2 = 0.0616
Largest diff. peak/hole / e Å⁻³	0.33/-0.31
Masked void volume / Å⁻³	109.2
Masked electrons	36.9
Masked void content	DMF

Identification Code	Compound 2
Empirical formula	$C_{21}H_{17}N_2O_5Zn$
Formula weight	442.73
Temperature/K	240.00(14)
Crystal system	Orthorhombic
Space group	*Pbam*
a/Å	16.4960(7)
b/Å	15.8918(6)
c/Å	11.4039(4)
α/°	90
β/°	90
γ/°	90
Volume/Å³	2989.5(2)
Z	4
ρ_{calc}g/cm³	0.984
μ/mm⁻¹	1.345
F(000)	908
Crystal size/mm³	0.2617 × 0.1137 × 0.0781
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.724 to 152.528
Index ranges	-18 ≤ h ≤ 20, -19 ≤ k ≤ 18, -9 ≤ l ≤ 14
Reflections collected	9529
Independent reflections	3241 [R_{int} = 0.0374, R_{sigma} = 0.0336]
Data/restraints/parameters	3241/139/240
Goodness-of-fit on F²	1.072
Final R indexes [I>=2σ (I)]	R1 = 0.0709, wR2 = 0.2156
Final R indexes [all data]	R1 = 0.0785, wR2 = 0.2223
Largest diff. peak/hole / e Å⁻³	0.67/-0.62
Masked void volume / Å⁻³	849.3
Masked electrons	226.1
Masked void content	DMF

Identification code	Compound 3
Empirical formula	$C_{21}H_{16}N_2O_5Zn$
Formula weight	441.73
Temperature/K	102.9(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3963(4)
b/Å	15.6396(6)
c/Å	16.3032(6)
α/°	90
β/°	96.459(4)
γ/°	90
Volume/Å³	2887.33(18)
Z	4
ρ_{calc}g/cm³	1.016
μ/mm⁻¹	1.393
F(000)	904
Crystal size/mm³	0.1763 × 0.0264 × 0.020
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.808 to 148.13
Index ranges	-11 ≤ h ≤ 14, -16 ≤ k ≤ 19, -18 ≤ l ≤ 20
Reflections collected	11609
Independent reflections	5693 [R_{int} = 0.0208, R_{sigma} = 0.0283]
Data/restraints/parameters	5693/14/305
Goodness-of-fit on F²	1.131
Final R indexes [I>=2σ (I)]	R1 = 0.0497, wR2 = 0.1589
Final R indexes [all data]	R1 = 0.0531, wR2 = 0.1616
Largest diff. peak/hole / e Å⁻³	0.93/-1.04
Masked void volume / Å⁻³	1211.7
Masked electrons	387.2
Masked void content	DMF

Identification Code	Compound 2_CID
Empirical formula	$C_{21}H_{18}N_2O_5Zn$
Formula weight	443.74
Temperature/K	106.3(5)
Crystal system	triclinic
Space group	*P*-1
a/Å	9.9902(4)
b/Å	11.4259(4)
c/Å	12.1064(5)
α/°	109.285(3)
β/°	108.208(4)
γ/°	97.690(3)
Volume/Å³	1194.97(9)
Z	2
ρ_{calc}g/cm³	1.233
μ/mm⁻¹	1.683
F(000)	456
Crystal size/mm³	0.302 × 0.1166 × 0.0627
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.37 to 148.378
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 14, -15 ≤ l ≤ 14
Reflections collected	8167
Independent reflections	4677 [R_{int} = 0.0265, R_{sigma} = 0.0326]
Data/restraints/parameters	4677/0/263
Goodness-of-fit on F²	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0846
Final R indexes [all data]	R_1 = 0.0332, wR_2 = 0.0864
Largest diff. peak/hole / e Å⁻³	0.51/-0.45
Masked void volume / Å⁻³	347.9
Masked electrons	97.2
Masked void content	DMF