Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

The Structural Diversity and Properties of Nine New Viologen based Zwitterionic Metal-Organic Frameworks

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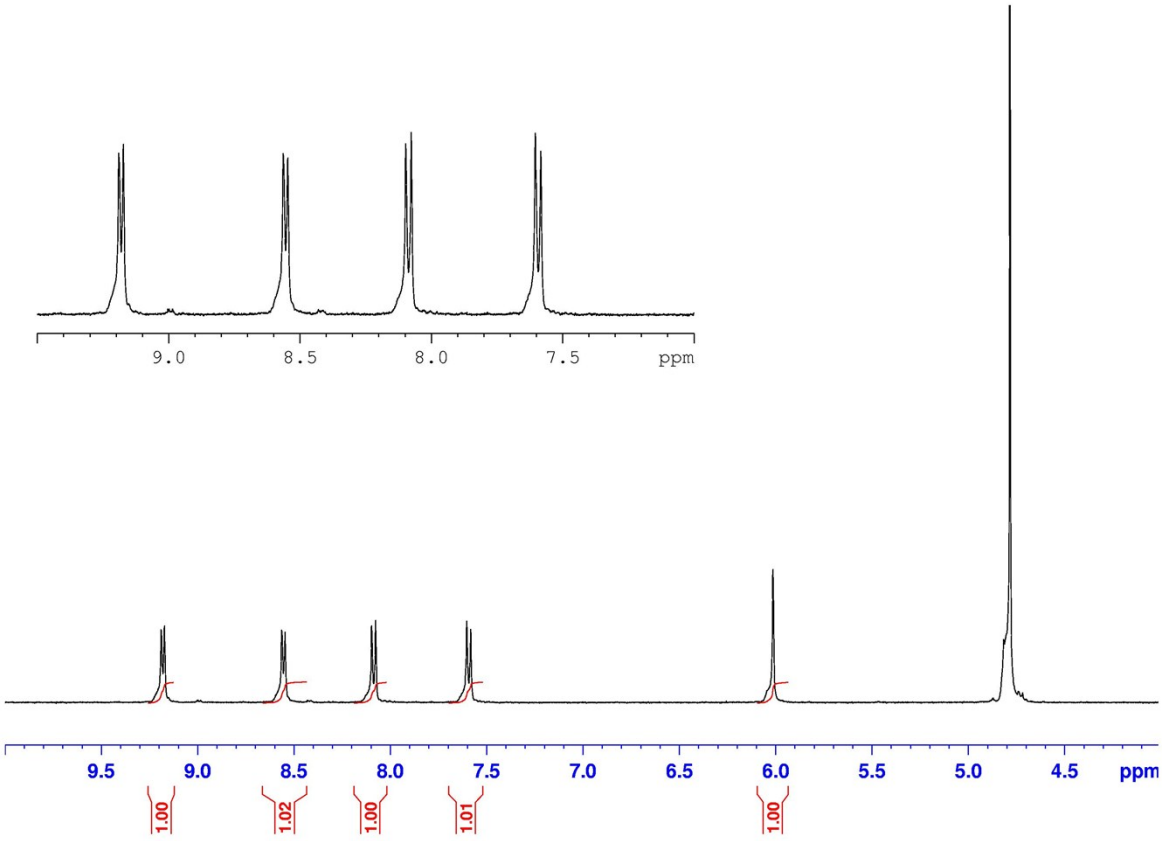

Figure S1. ^{1}H NMR of **L** in D_2O.

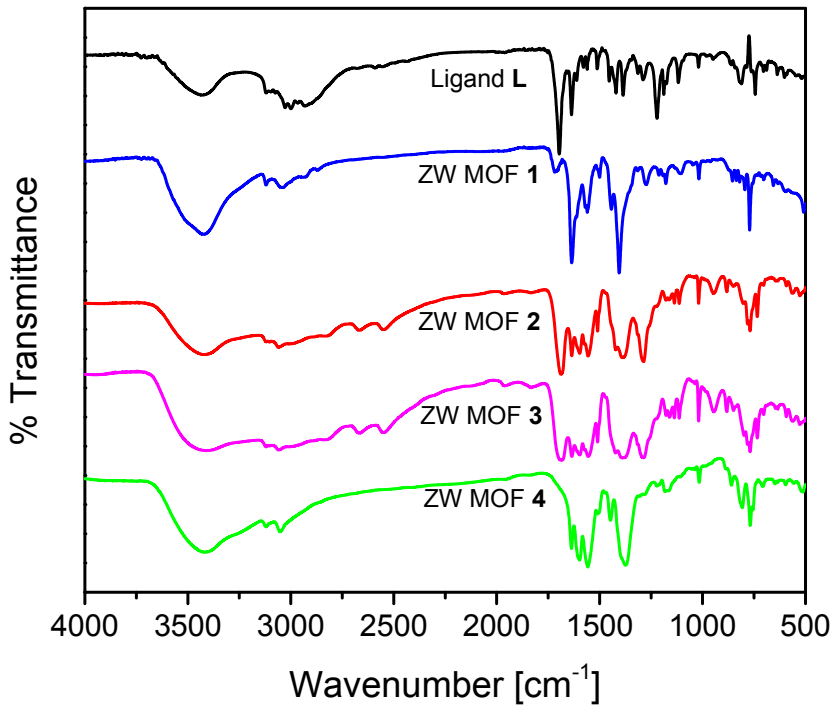

Figure S2. IR data of ligand **L** (black), ZW MOF **1** (blue), **2** (red), **3** (magenta) and **4** (green). Characteristic peaks: $\tilde{\nu}$ = 3300-3250 (O-H stretch, water), 3100-3000 (C-H stretch, aromatics), 1760-1690 (C=O stretch, carboxylate), 1600-1585 (C-C stretch, aromatics), 1335-1250 (C-N stretch), 1320-1000 (C-O stretch, carboxylate), 950-910 (O-H bend, water).

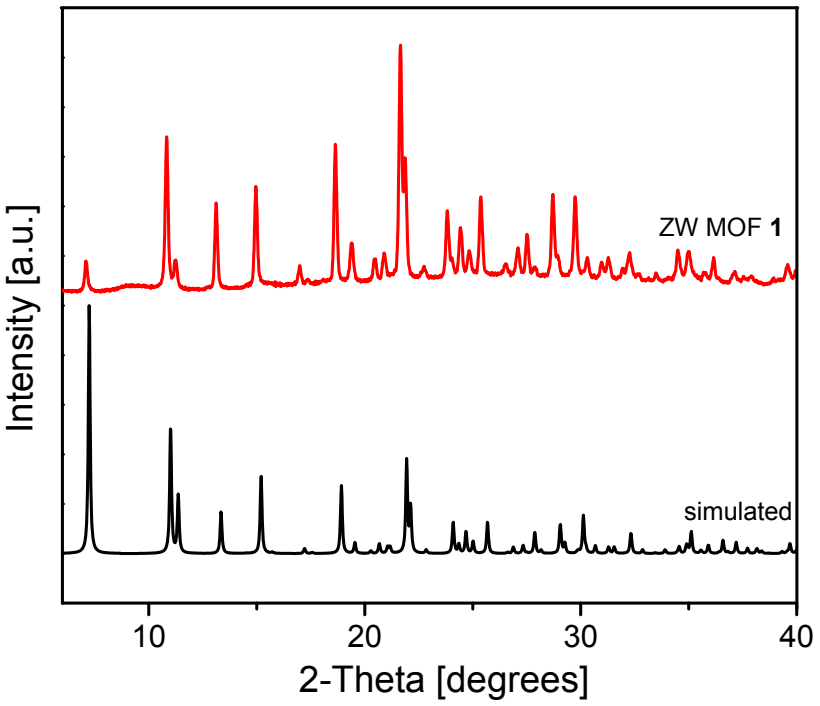

Figure S3. Powder X-ray diffraction patterns for simulated (black) and as-synthesized (red) forms of ZW MOF **1**.

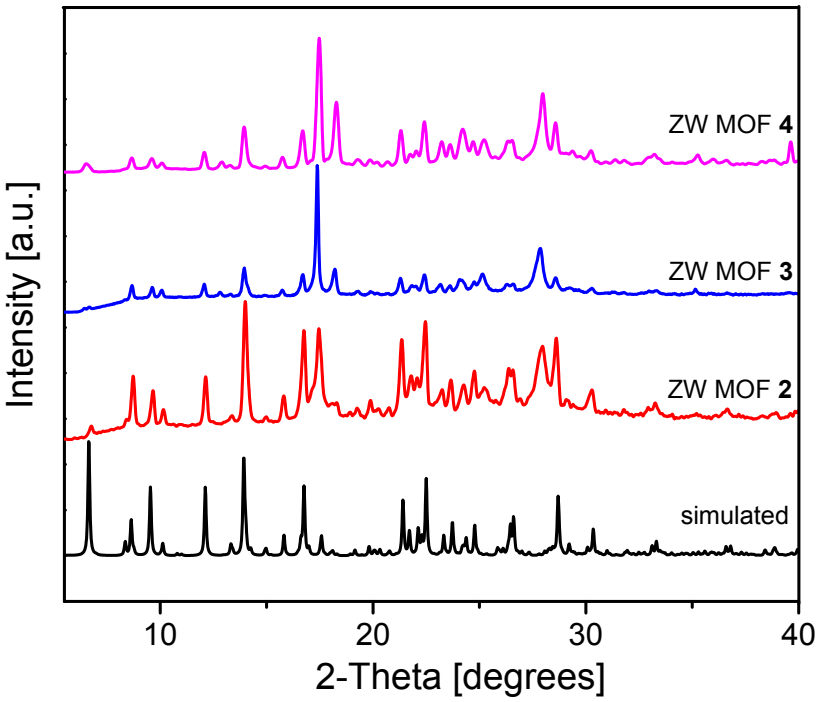

Figure S4. Powder X-ray diffraction patterns for simulated (black) and as-synthesized forms of ZW MOFs **2** (red), **3** (blue) and **4** (magenta).

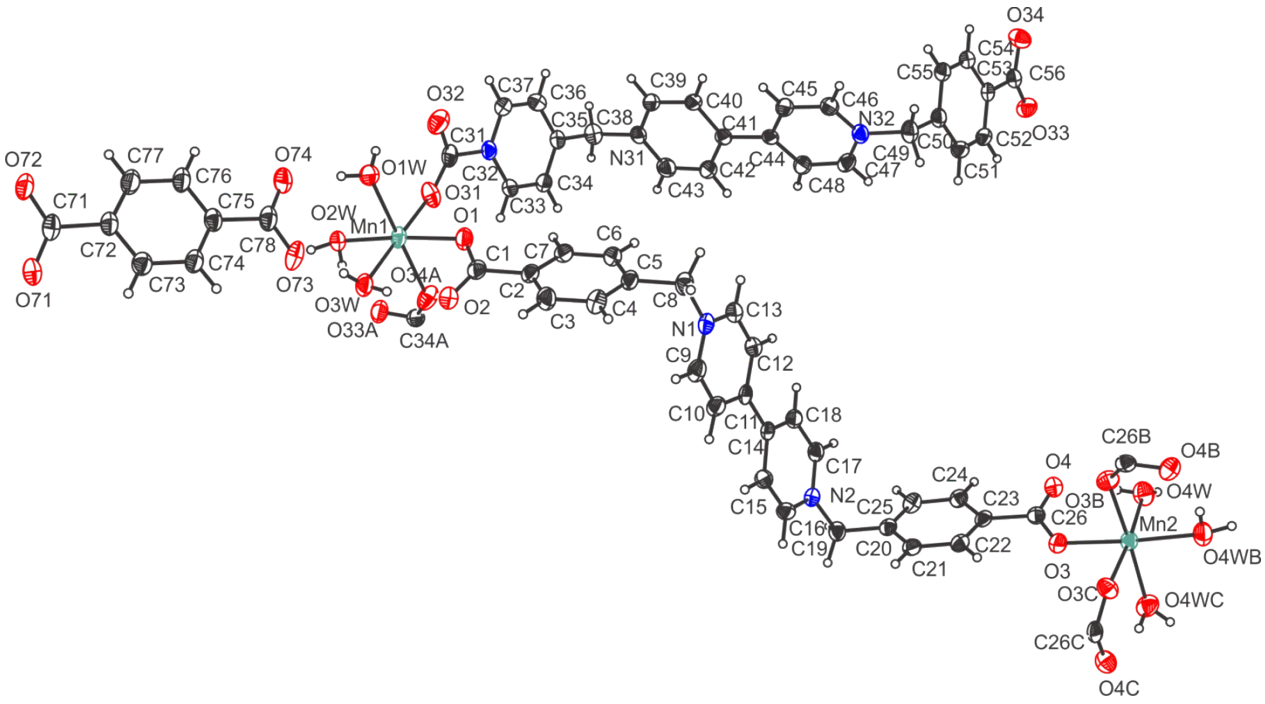

Figure S5. Crystal structure of ZW MOF **2** with view of the coordination sphere of the Co(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry codes: A = 0.66 + y, 0.33 – x + y, 0.33 – z; B = -x + y, -x, z; C = -y, x – y, z.

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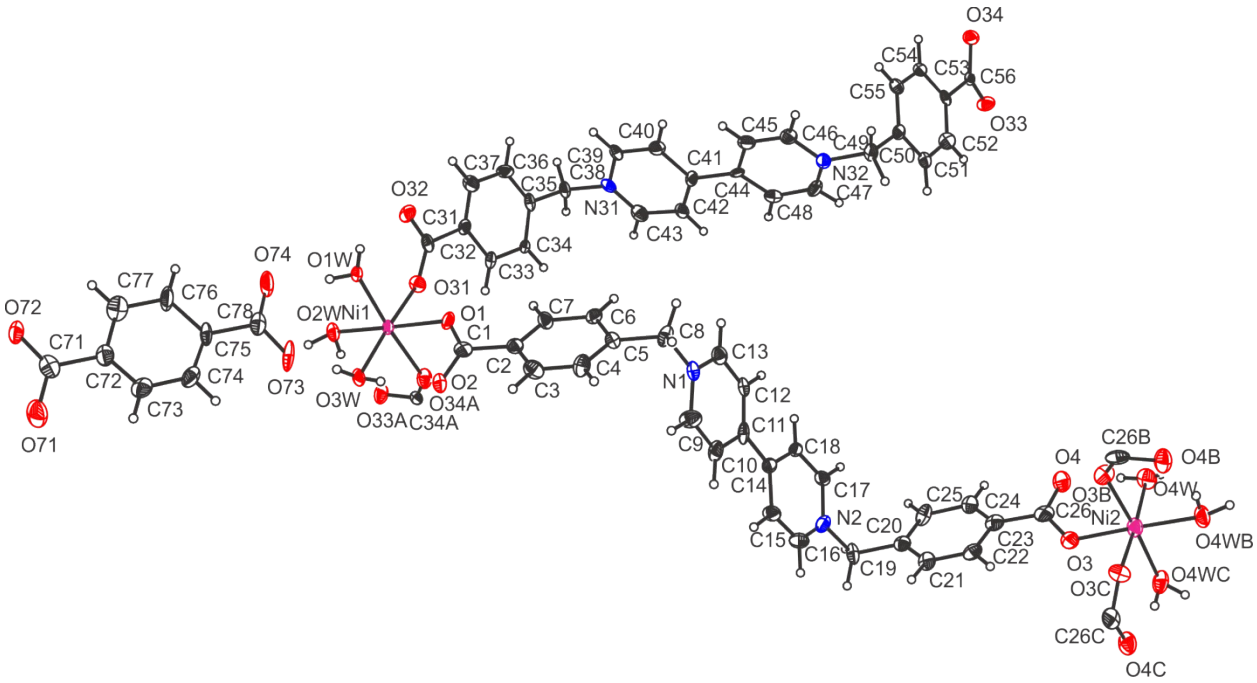

Figure S6. Crystal structure of ZW MOF **4** with view of the coordination sphere of the Ni(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry codes: A = y, -x + y, -z + 1; B = -y + 1, x – y, z; C = -x + y + 1, -x + 1, z.

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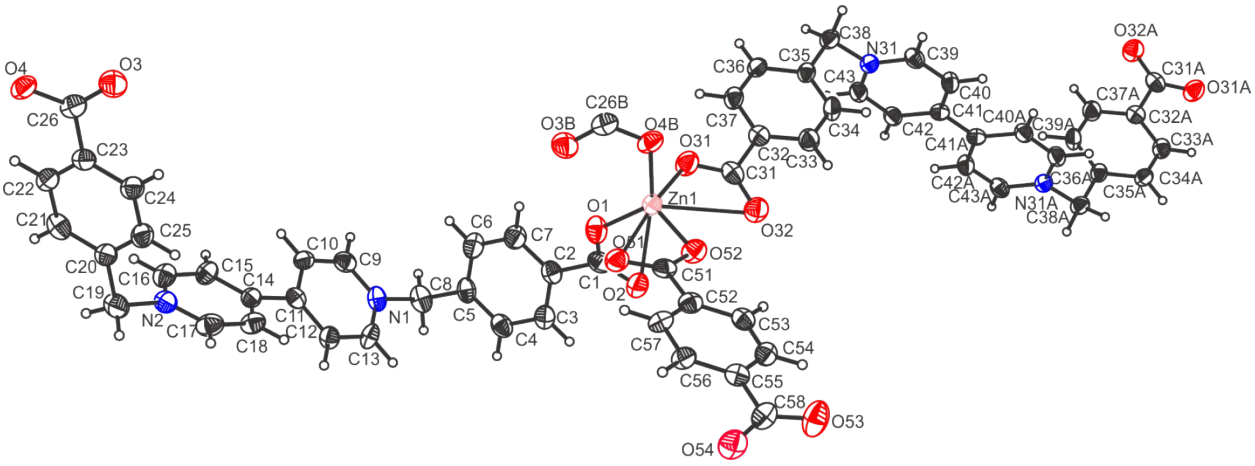

Figure S7. Crystal structure of ZW MOF **6** with view of the coordination sphere of the Zn(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry codes: A = -x – 1, -y – 1, -z + 1.

Table S1. Characteristic distances and angles of hydrogen bonding interactions in ZW MOF **7.**

D–H	***d*(H···A) [Å]**	**<DHA [deg]**	***d*(D···A) [Å]**	**A**
C30-H30	2.670	139.00	3.444	N11 [x – 1, y, z]
C30-H30	2.613	124.28	3.245	O22 [x – 1, y, z]
C35-H35	2.694	129.51	3.378	N2 [x – 1, y, z]
C33-H33	2.631	160.39	3.540	N1 [-x, y + 1/2, -z + 1/2]
C35-H35	2.535	131.18	3.241	O23 [x + 1, y, z]
C37-H37	2.384	155.55	3.272	O7WA [-x, y + 1/2, -z + 1/2]
O1W-H1WB	2.079	155.76	2.866	O5WA
O1W-H1WA	2.046	149.98	2.805	O3WA [-x + 1, -y, -z]
O2W-H2WA	1.934	168.89	2.763	O12
O2W-H2WB	2.048	152.57	2.820	O23 [x + 2, -y + 1/2, z – 1/2]
O3WA-H3WAA	2.011	143.13	2.730	O2W
O3WA-H3WBA	2.304	138.50	2.985	O11 [-x + 1, -y, -z]
O4WA-H4WAA	1.966	164.10	2.783	O22
O4WA-H4WBA	1.961	161.66	2.771	O2 [x, -y + 1/2, z – 1/2]
O5WA-H5WAA	1.983	149.72	2.741	O6WA
O5WA-H5WBA	2.069	159.56	2.871	O7WA [x – 1, y, z]
O6WA-H6WAA	1.977	171.27	2.811	O4WA [-x, y – 1/2, -z + 1/2]
O6WA-H6WBA	2.148	157.22	2.941	O24 [x + 1, y, z]

Table S2. Characteristic distances and angles of hydrogen bonding interactions in **9**.

D–H	*d*(H···A) [Å]	<DHA [deg]	*d*(D···A) [Å]	A
O2-H2	1.810	162.39	2.623	O1W
C8-H8B	2.522	145.61	3.385	O1 [x – 1, y, z]
C9-H9	2.480	152.17	3.349	O1 [x – 1, y, z]
C10-H10	2.557	126.74	3.216	O2 [-x, -y + 1, -z]
C13-H13	2.569	112.75	3.064	O21 [x, y, z – 1]
C13-H13	2.408	122.57	3.028	O21 [-x + 1, -y, -z]
O1W-H1WA	2.203	143.69	2.923	O22 [x, y + 1, z]
O1W-H1WB	2.620	162.01	3.429	Br1 [x + 1, y, z]

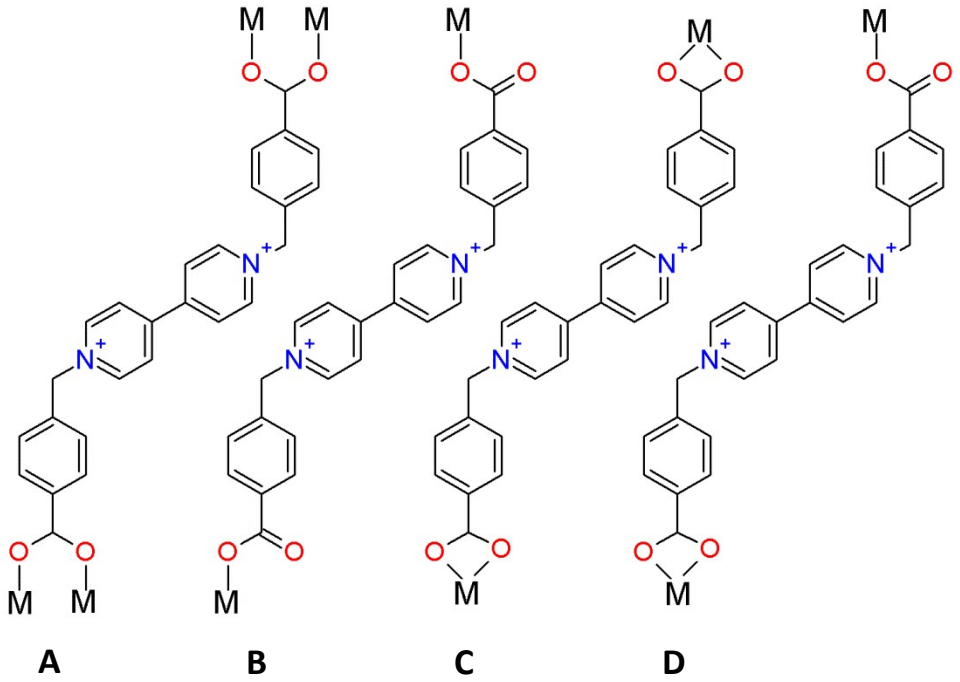

Figure S8. Various coordination modes of **L** found in compounds **1-9:** (A) μ_4-η^1:η^1:η^1:η^1; (B) μ_2-η^1:η^1; (C) μ_2-η^2:η^2; and (D) μ_2-η^2:η^1.

Single crystal structure analysis, comments on checkcif B alerts

All B-alerts can be grouped into four categories:

a) Short intermolecular H_{water}-H_{water} and O_{water}-O_{water} contacts. Answer: These hydrogens were located in the electron density map; hence, these alerts do not stem from inconsistencies of the crystal structures.

b) Isolated oxygen atom found in crystal structure. Answer: Disordered water oxygen atoms could be refined only isotropically for which additionally no hydrogen atoms could be found in the electron density map; hence, these alerts do not stem from inconsistencies of the crystal structures.

c) Hydrogen water atoms without acceptor. Answer: All significant residual electron densities could be assigned to water molecules, and thus, no missing acceptor atoms can be found; hence, these alerts do not stem from inconsistencies of the crystal structures.

d) Low completeness. Answer: This alert was found only in MOF **9** with a completeness of 0.958 and is a result of a very weak diffracting crystal. Several crystals have been screened with no better output and also attempts made to grow better quality crystals have not been successful. However, our reported completeness of 0.958 lies well within the IUCR acceptable limits for publishing crystal structures.

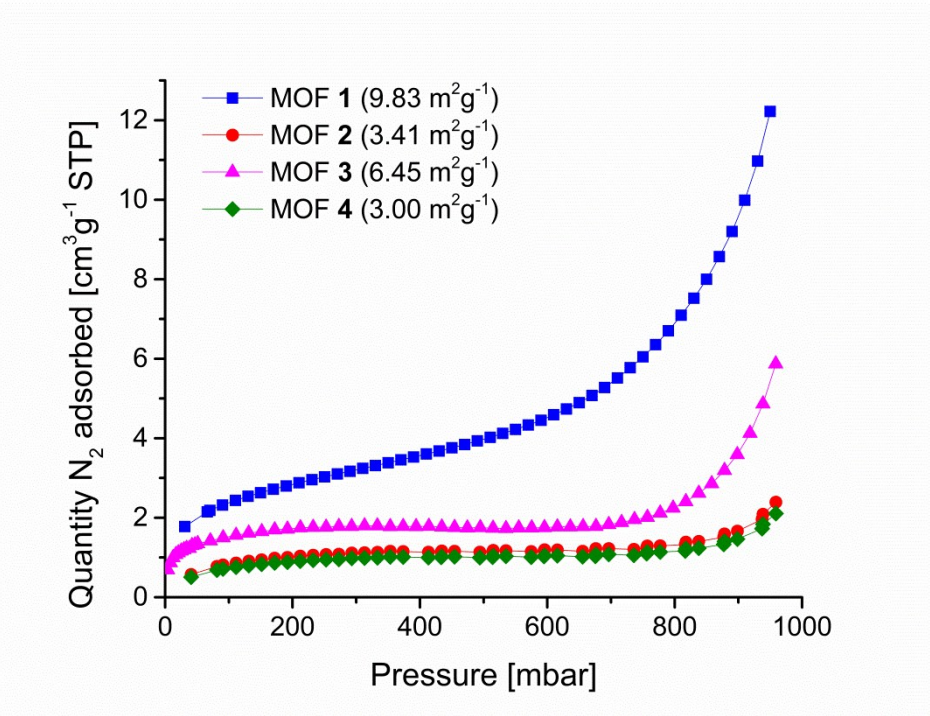

Figure S9. Nitrogen adsorption isotherms collected at 77 K for **1** (blue squares), **2** (red circles), **3** (majenta triangles) and **4** (green diamonds). BET surface area values are labelled.

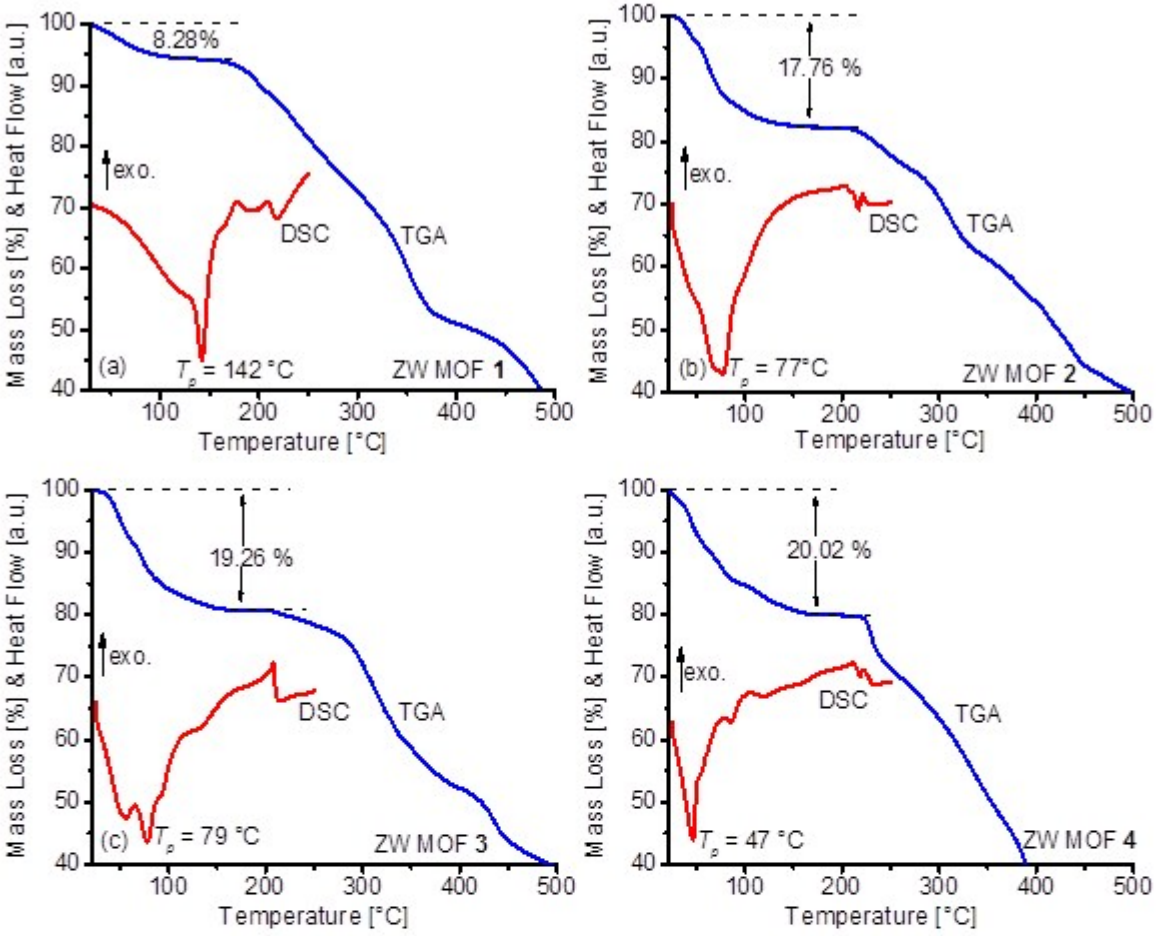

Figure S10. TGA and DSC curves for ZW MOFs **1** (A), **2** (B), **3** (C), **4** (D). Heating rate = 3 °C·min^{-1}; given are the peak temperatures T_P [°C].