ELECTRONIC SUPPORTING INFORMATION

Flexible Lanthanide MOFs as Highly Selective and Reusable Liquid MeOH Sorbents

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Table S1. Selected crystal data for **UCY-4–UCY-8** , **UCY-5**/MeOH and **UCY-5**/acetone

Compound	**UCY-4**	**UCY-5**	**UCY-5**/MeOH	**UCY-5**/acetone	**UCY-6**	**UCY-7**	**UCY-8**
Chemical formula	$C_{22}H_{20}LaN_3O_8$	$C_{22}H_{20}CeN_3O_8$	$C_{69}H_{47}Ce_4N_4O_{32}$	$C_{19}H_{14}CeNO_9$	$C_{22}H_{20}N_3O_8Pr$	$C_{41}H_{34}N_5O_{16}Sm_2$	$C_{19}H_{14}EuN_2O_8$
Formula Mass	593.32	594.53	2004.59	540.43	595.32	1153.45	550.28
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	29.074(2)	29.049(2)	28.667(4)	33.657(2)	28.877(2)	28.808(2)	29.255(2)
b/Å	14.5356(5)	14.5685(6)	14.910(2)	14.2909(5)	14.3145(9)	14.3140(7)	12.699(2)
c/Å	13.5095(5)	13.5097(7)	12.013(2)	12.8304(9)	13.635(2)	13.5515(6)	14.260(2)
β/°	100.097(5)	100.119(5)	106.27(2)	124.037(9)	99.644(9)	99.776(4)	97.522(8)
Unit cell volume/Å^3	5620.8(4)	5628.4(4)	4929(2)	5114.0(7)	5556.4(8)	5507.0(4)	5252.2(9)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*
No. of formula units per unit cell, *Z*	8	8	2	8	8	4	8
Radiation type	MoKα	MoKα	CuKα	MoKα	MoKα	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	1.563	1.661	14.585	1.821	1.797	2.173	17.439
No. of reflections measured	12896	14490	8129	19630	10719	13354	9887
No. of independent reflections	4946	5942	4364	5289	5458	5689	4665
R_{int}	0.0429	0.0359	0.0353	0.0372	0.0416	0.0326	0.0527
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0473	0.0575	0.0576	0.0409	0.0674	0.0461	0.0718
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[b]	0.1438	0.1493	0.1666	0.1238	0.2086	0.1334	0.2025
Final R_1 values (all data)[a]	0.0526	0.0723	0.0623	0.0471	0.0889	0.0609	0.0842
Final $wR(F^2)$ values (all data)[b]	0.1485	0.1567	0.1718	0.1283	0.2280	0.1414	0.2199
Goodness of fit on F^2	1.084	1.069	1.151	1.090	1.150	1.109	1.098

[a] $R_1=\Sigma \| Fo | - | Fc \| / \Sigma | Fo |$. [b] $wR(F^2)=[\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[wF_o^2)2]]^{1/2}$, $w=1/[\sigma^2(F_o^2) + (m \bullet p)^2 + n \bullet p]$, $p=[max(F_o^2,0) + 2F_c^2]/3$, and m and n are constants

Table S2. Selected crystal data for compounds **UCY-9 –UCY-12**

Compound	**UCY-9**	**UCY-10**	**UCY-11**	**UCY-12**
Chemical formula	$C_{82}H_{68}Gd_4N_{10}O_{32}$	$C_{19}H_{14}N_2O_8Tb$	$C_{19}H_{14}DyN_2O_8$	$C_{82}H_{68}Ho_4N_{10}O_{32}$
Formula Mass	2334.46	557.24	560.82	2365.18
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	28.747(2)	29.157(2)	28.7897(8)	28.675(2)
b/Å	14.448(2)	13.090(2)	13.9077(7)	14.3540(7)
c/Å	13.3233(8)	13.9533(9)	13.6093(5)	13.347(2)
α/°	90.00	90.00	90.00	90.00
β/°	99.760(7)	97.576(6)	99.074(3)	99.650(6)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	5453.5(6)	5279.1(7)	5380.9(4)	5415.8(6)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*
No. of formula units per unit cell, *Z*	2	8	8	2
Radiation type	CuKα	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	16.095	2.717	2.814	2.962
No. of reflections measured	9376	13876	12896	18439
No. of independent reflections	4854	4650	4727	4749
R_{int}	0.0554	0.0531	0.0481	0.0475
Final R_1 values ($I > 2\sigma(I)$)	0.0750	0.0445	0.0855	0.0864
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2065	0.1133	0.2660	0.2292
Final R_1 values (all data)	0.0877	0.0649	0.0990	0.0925
Final $wR(F^2)$ values (all data)	0.2199	0.1210	0.2738	0.2318
Goodness of fit on F^2	1.066	0.958	1.134	1.031

[a] $R_1=\Sigma \| Fo | - | Fc \| / \Sigma | Fo |$. [b] $wR(F^2)=[\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[wF_o^2)2]]^{1/2}$, $w=1/[\sigma^2(F_o^2) + (m \bullet p)^2 + n \bullet p]$, $p=[\max(F_o^2,0) + 2F_c^2]/3$, and m and n are constants

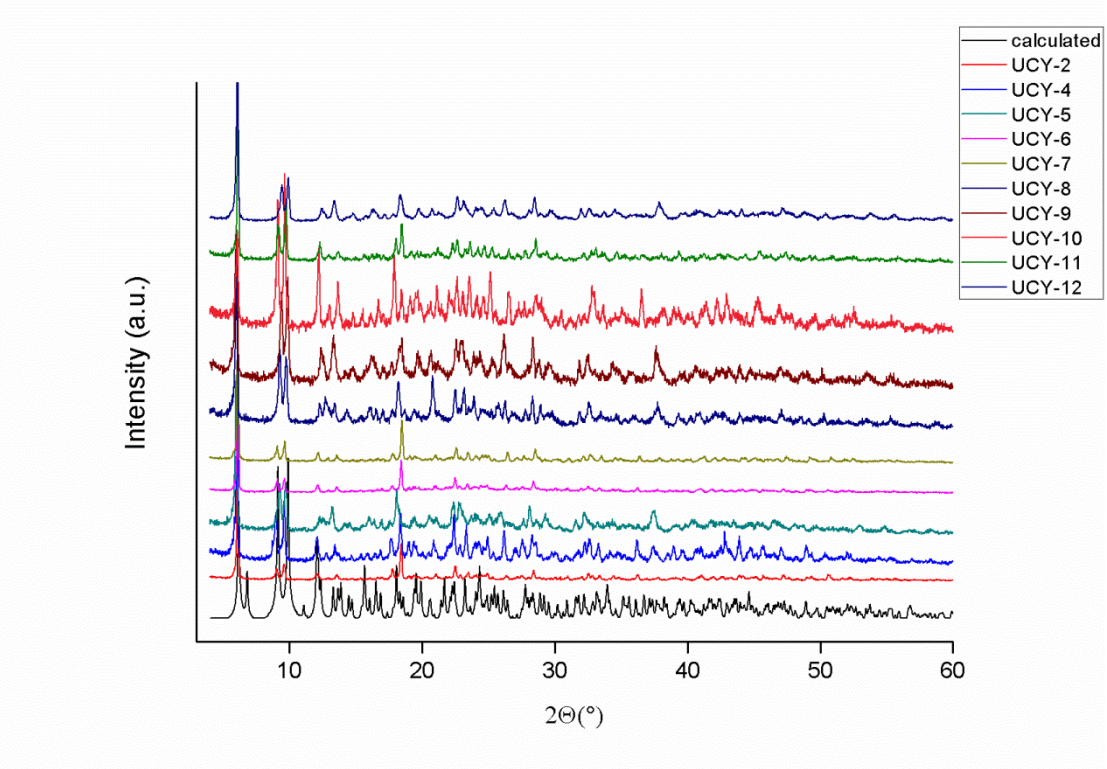

Fig. S1 Experimental and calculated PXRD patterns of **UCY-2, UCY-4-UCY-12**.

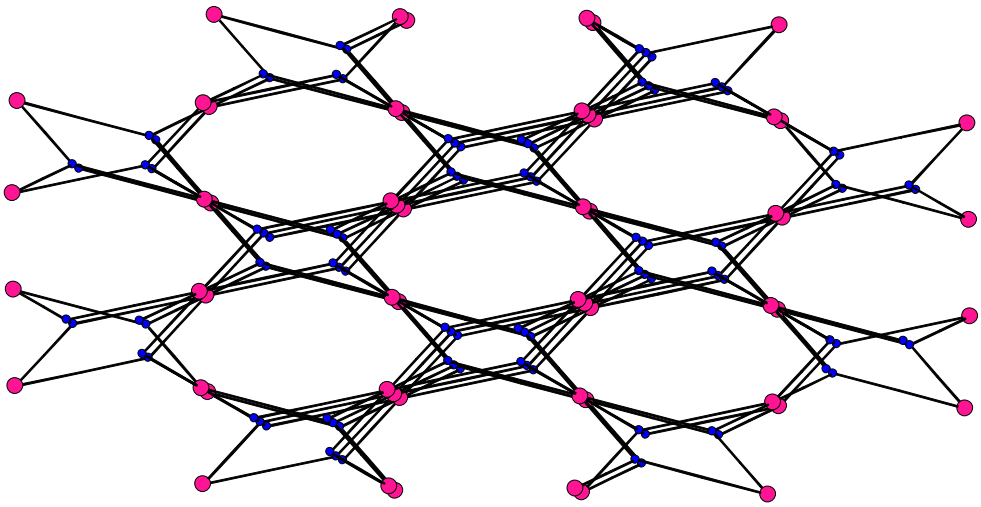

Fig. S2 Representation of the flu-3,6-C2/c topology of **UCY-2, UCY-4-UCY-12.**. Pink and blue spheres represent the 6-c and 3-c nodes, respectively.

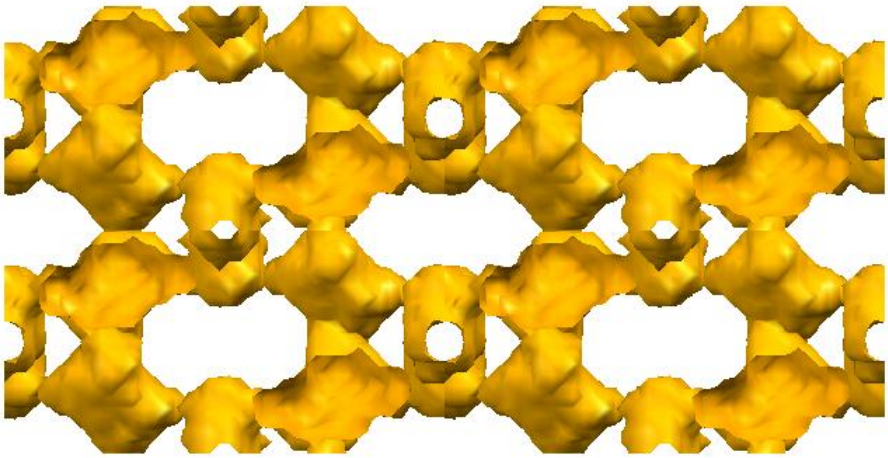

Fig. S3 Representation of the pore network of **UCY-4**.

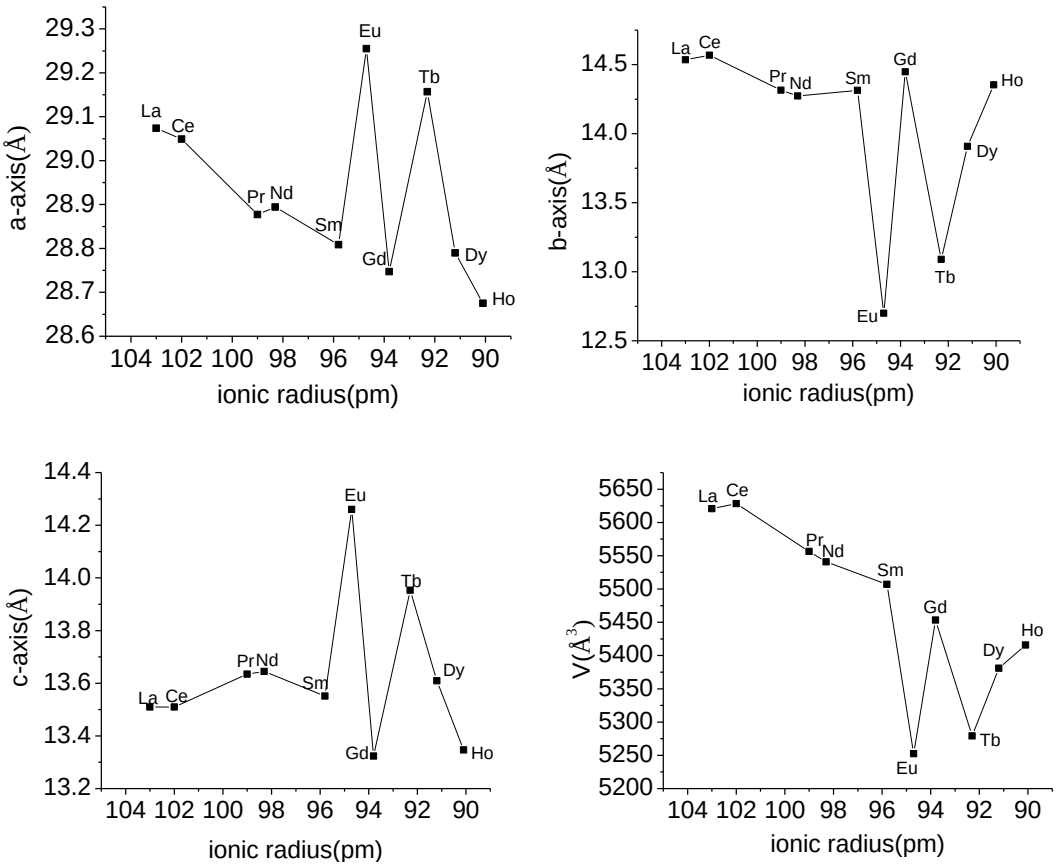

Fig. S4 Plots of the cell parameters of **UCY-4** (La), **UCY-5** (Ce), **UCY-6** (Pr), **UCY-2** (Nd), **UCY-7** (Sm), **UCY-8** (Eu), **UCY-9** (Gd), **UCY-10** (Tb), **UCY-11** (Dy) and **UCY-12** (Ho) vs. the lanthanide ionic radii.

Thermal Stability data

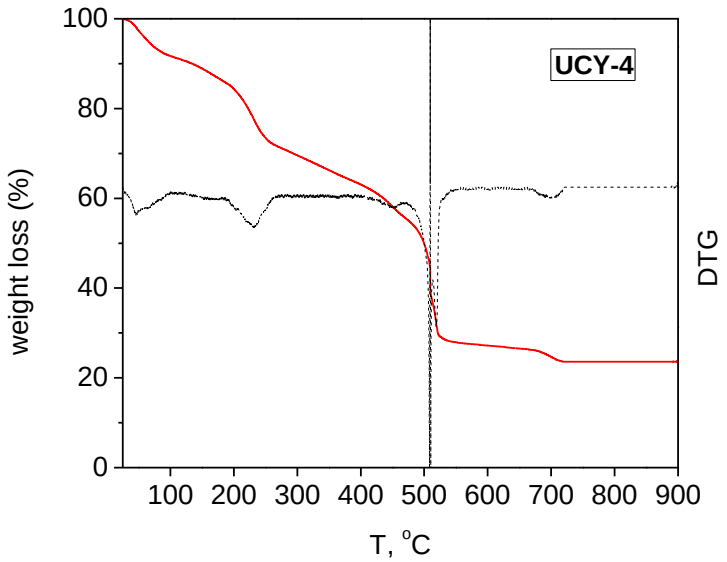

Fig. S5 The TG (red)/DTG (dashed line) curves for compound **UCY-4**.

UCY-4: The initial losses occurring from 30-275 °C are due to the elimination of 4 H_2O and 4 DMF molecules (calculated loss = 28.9%; found = 28.8%). The following weight losses (47.5 %), which end at ~ 716 °C, are attributed to the release of the CIP ligands (calculated loss: 49.1%).

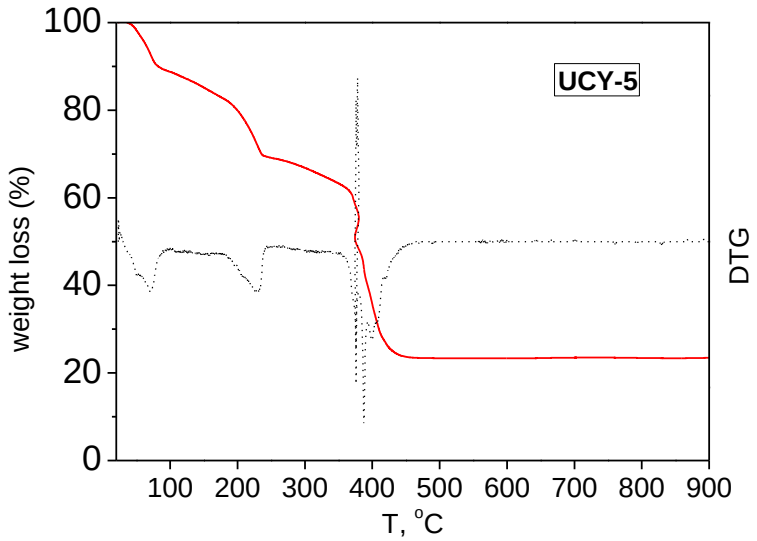

Fig. S6 The TG (red)/DTG (dashed line) curves for compound **UCY-5**.

UCY-5: The initial losses occurring from 30-250 °C are assigned to the removal of 6 H_2O and 4 DMF molecules (calculated loss = 30.8 %; found = 30.9 %). The following weight losses (45.6 %), which end at ~ 456 °C, are due to the release of the CIP ligands (calculated loss: 47.7 %).

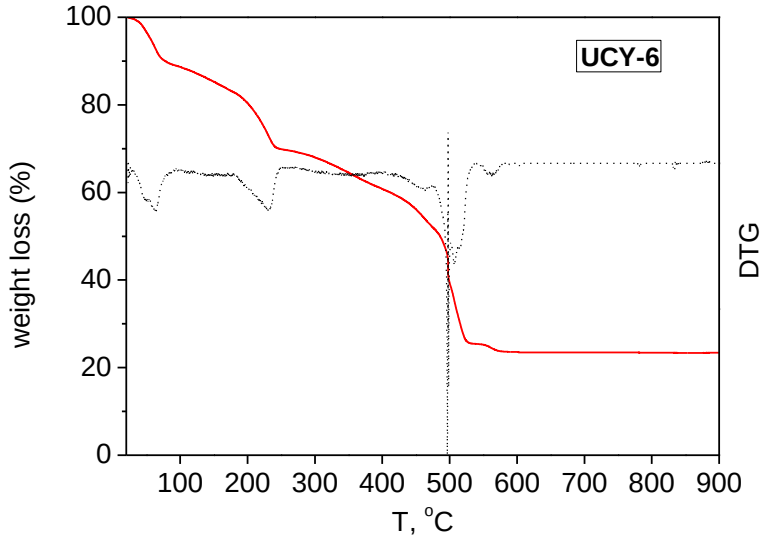

Fig. S7 The TG (red)/DTG (dashed line) curves for compound **UCY-6**.

UCY-6: The initial losses occur from 30-255°C and are ascribed to the elimination of 5.5 H_2O and 4 DMF molecules (calculated loss = 30.2%; found = 30.3%). The following weight losses (46.1%), which end at ~ 580 °C, are due to the release of the CIP ligands (calculated loss: 48.0 %).

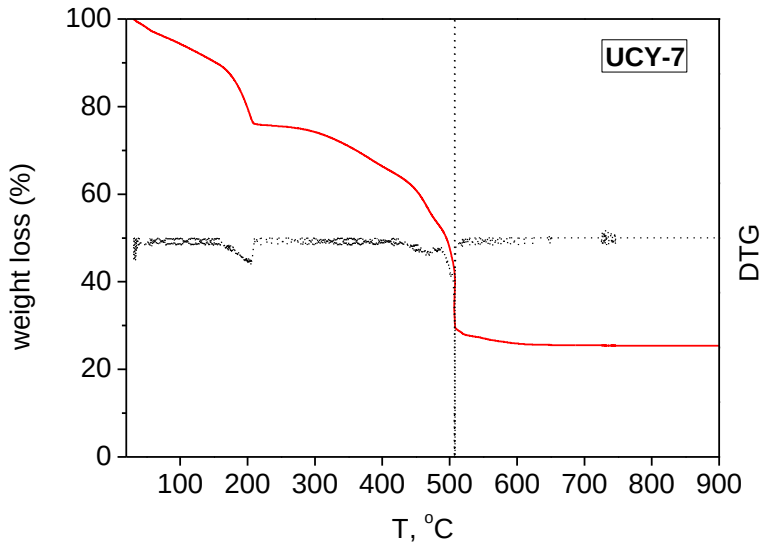

Fig. S8 The TG (red)/DTG (dashed line) curves for compound **UCY-7**.

UCY-7: The initial losses occurring from 30-214 °C are due to the elimination of 4 H_2O and 3 DMF molecules (calculated loss = 24.0 %; found = 24.1 %). The following weight losses (50.4 %), which end at ~ 650 °C, are attributed to the release of the CIP ligands (calculated loss: 51.2 %).

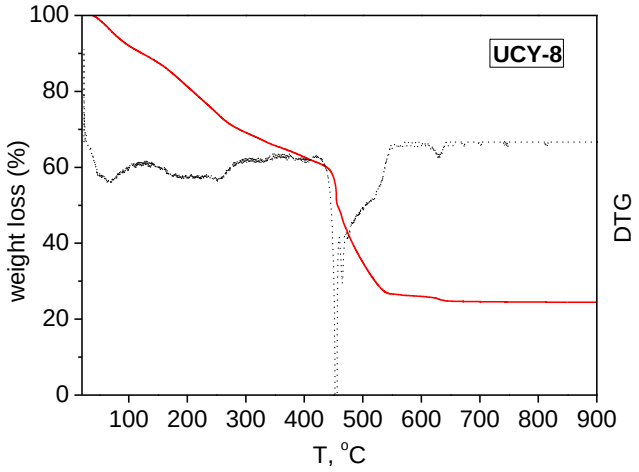

Fig. S9 The TG (red)/DTG (dashed line) curves for compound **UCY-8**.

UCY-8: The initial losses occurring from 30-300 °C are due to the elimination of 6.5 H_2O and 4 DMF molecules (calculated loss = 30.9 %; found = 30.7 %). The following weight losses (44.4 %), which end at ~ 653 °C, are attributed to the release of the CIP ligands (calculated loss: 46.5 %).

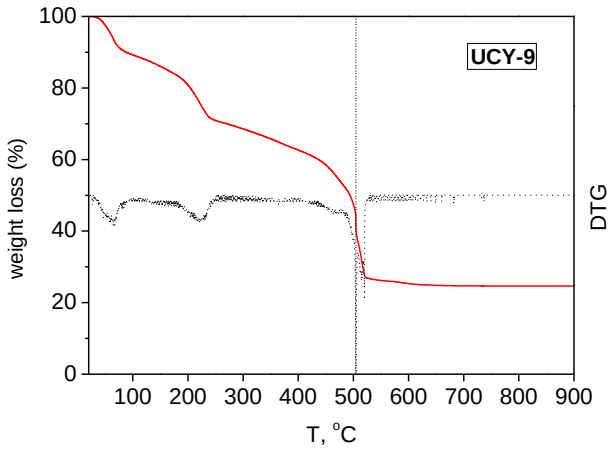

Fig. S10 The TG (red)/DTG (dashed line) curves for compound **UCY-9**.

UCY-9: The initial losses occurring from 30-253 °C are due to the elimination of 5.5 H_2O and 4 DMF molecules (calculated loss = 29.5 %; found = 29.2 %). The following weight losses (46.0

%), which end at ~ 650 °C, are attributed to the release of the CIP ligands (calculated loss: 46.5 %).

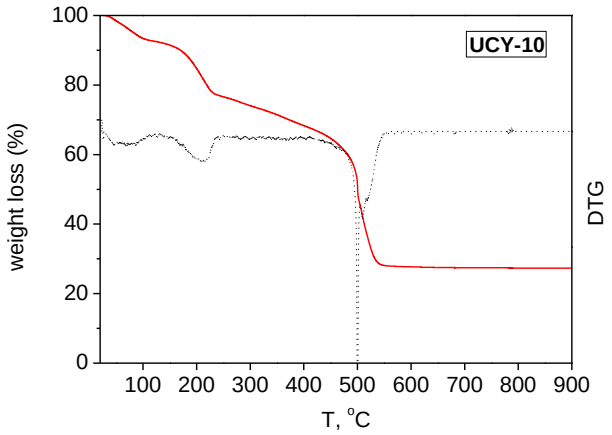

Fig. S11 The TG (red)/DTG (dashed line) curves for compound **UCY-10**.

UCY-10: The initial losses occurring from 30-240 °C are due to the elimination of 7.5 H_2O and 2 DMF molecules (calculated loss = 23.1 %; found = 23.0 %). The following weight losses (49.4 %), which end at ~ 600 °C, are attributed to the release of the CIP ligands (calculated loss: 50.9 %).

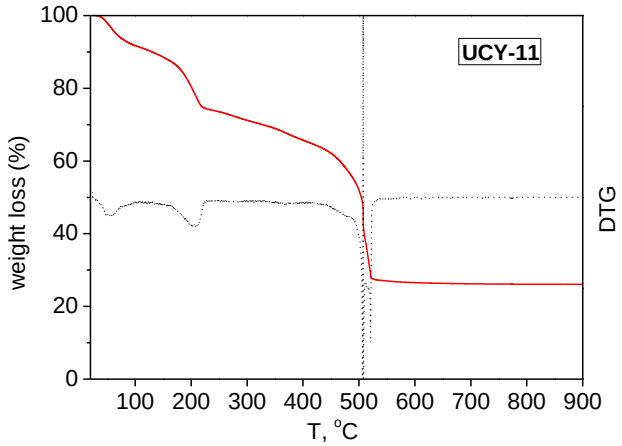

Fig. S12 The TG (red)/DTG (dashed line) curves for compound **UCY-11**.

UCY-11: The initial losses occurring from 30-235 °C are due to the elimination of $6H_2O$ and 3DMF molecules (calculated loss = 25.7 %; found = 25.9 %). The following weight losses (47.7 %), which end at ~ 647 °C, are attributed to the release of the CIP ligands (calculated loss: 48.8 %).

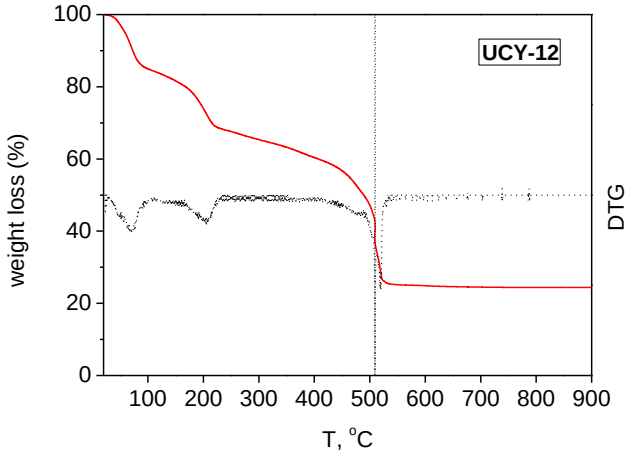

Fig. S13 The TG (red)/DTG (dashed line) curves for compound **UCY-12**.

UCY-12: The initial losses occurring from 30-233 °C are due to the elimination of 8 H_2O and 4 DMF molecules (calculated loss = 31,7 %; found = 31.5 %). The following weight losses (43.7 %), which end at ~ 640 °C, are attributed to the release of the CIP ligands (calculated loss: 44.7 %).

MeOH adsorption data

A. Data for the calculation of the sorption isotherm

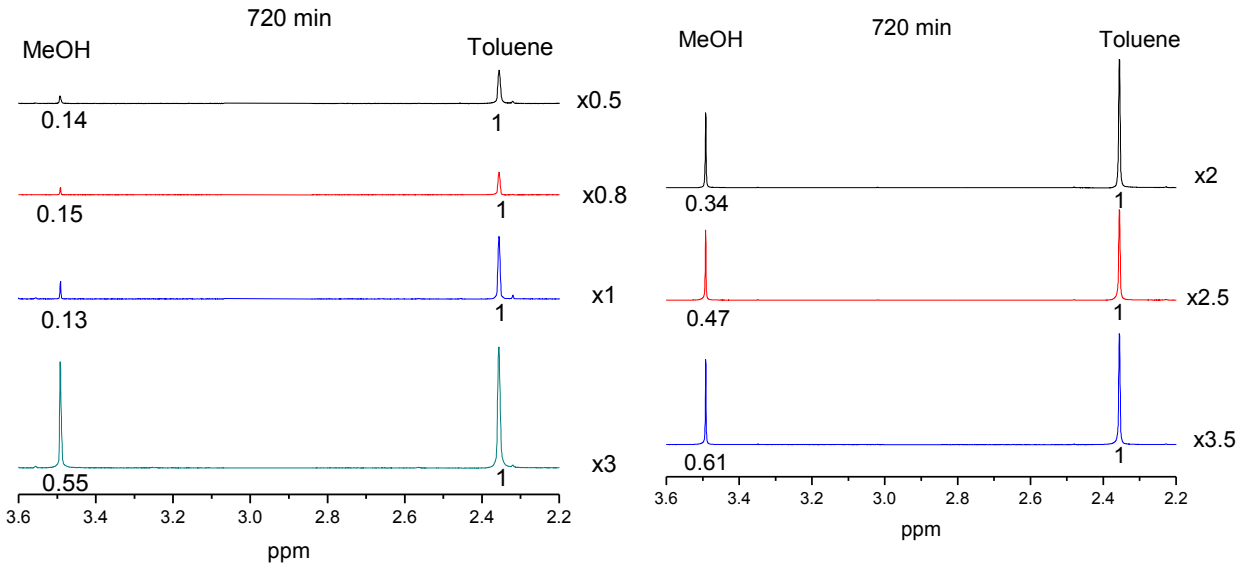

Fig. S14 ^{1}H-NMR spectra in CD_3Cl of the supernatant liquids resulted from the reactions of **UCY-5**/dry with MeOH in various molar ratios (various equivalents of MeOH per mol of **UCY-5**/dry) for an adsorption time of ~12 h. The numbers under each peak represent the values of the peak integrals. In the initial solutions used (i.e. before the sorption process) the ratio of peak integrals was equal to 1. The exact quantities of the reactants in the various reactions performed are: *x0.5* [MeOH (4.5 μL,3.56 mg,0.111 mmol,0.5 eq.), toluene (11.75 μL,10.25 mg,0.111 mmol), **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl], *x0.8* [MeOH (7.2 μL, 5.69 mg, 0.178 mmol, 0.8 eq.), toluene (18.8 μL,16.4 mg,0.178 mmol) and **UCY-5**/dry (0.1 g, 0.222mmol) in 4mL CD_3Cl], *x1* [MeOH (9 μL, 7.11 mg, 0.222 mmol,1 eq.), toluene (23. 5 μL,20.5mg,0.222mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl], *x2* [MeOH (18 μL,14.22mg,0.444 mmol, 2 eq.), toluene (47 μL, 41.0 mg, 0.444 mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl], *x2.5* [MeOH (22.5 μL, 17.78mg, 0.555 mmol 2.5 eq.), toluene (58.75 μL/51.25 mg/0.555 mmol), **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl], *x3* [MeOH (27 μL,21.33 mg,0.666 mmol, 3

eq.), toluene (70.5 μL, 61.5 mg, 0.666 mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl] and *x3.5* [MeOH (31.5 μL, 24.89 mg, 0.777 mmol, 3.5 eq.), toluene (82.25 μL, 71.75 mg, 0.777 mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl].

The peaks at 2.35 ppm and 3.49 ppm correspond to the methyl groups of toluene and MeOH respectively. The concentrations of MeOH after the sorption processes were determined using as reference the toluene that is not absorbed by **UCY-5**/dry at these reaction conditions (i.e magnetic stirring at room temperature and atmospheric pressure) and thus its concentration remains unchanged after the treatment of the solution with **UCY-5**/dry**.** For each experiment, the initial concentrations of MeOH and toluene were equal (i.e. the ratio of the peak integrals for the methyl groups of toluene and MeOH were equal to 1 in the ^{1}H-NMR spectra of the initial solutions).

B. PXRD studies

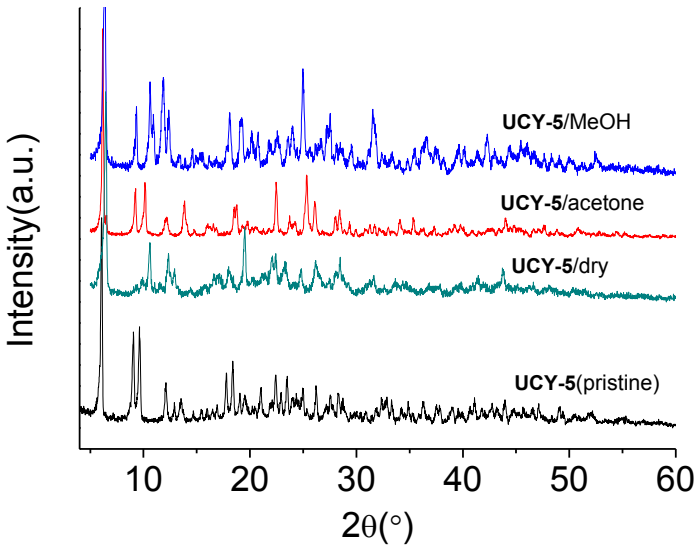

Fig. S15 PXRD patterns of **UCY-5** (pristine), **UCY-5**/dry, **UCY-5**/acetone and **UCY-5**/MeOH.

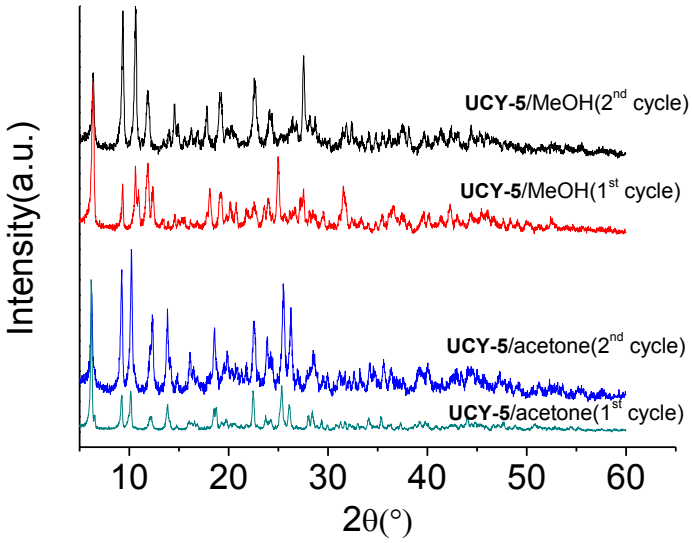

Fig. S16 PXRD patterns of **UCY-5**/MeOH prepared from original **UCY-5**/dry (**UCY-5**/MeOH 1st cycle), **UCY-5**/MeOH prepared from regenerated **UCY-5**/dry (**UCY-5**/MeOH 2nd cycle), **UCY-5**/acetone prepared from original **UCY-5**/dry (**UCY-5**/acetone 1st cycle) and **UCY-5**/acetone prepared from regenerated **UCY-5**/dry (**UCY-5**/acetone 2nd cycle).

C. Kinetic experiments

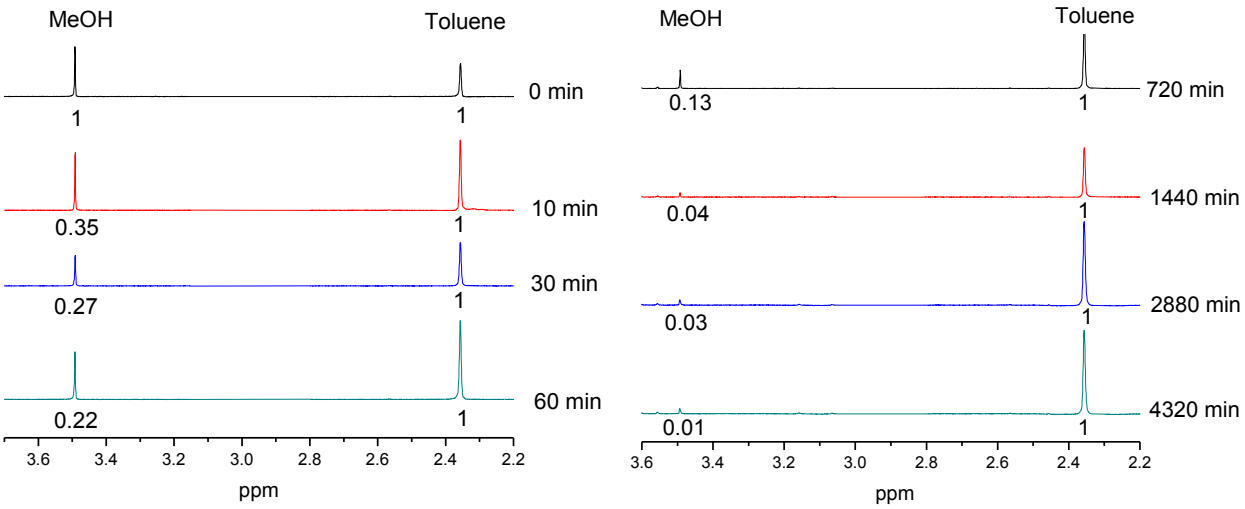

Fig. S17 ^{1}H-NMR spectra in CD_3Cl of aliquots taken at various adsorption times from suspensions containing equimolar initial amounts of MeOH (9 μL/7.11 mg/0.222 mmol, 1 eq.), toluene (23. 5 μL, 20.5mg, 0.222mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in CD_3Cl (4mL). The numbers under each peak represent the values of the peak integrals.

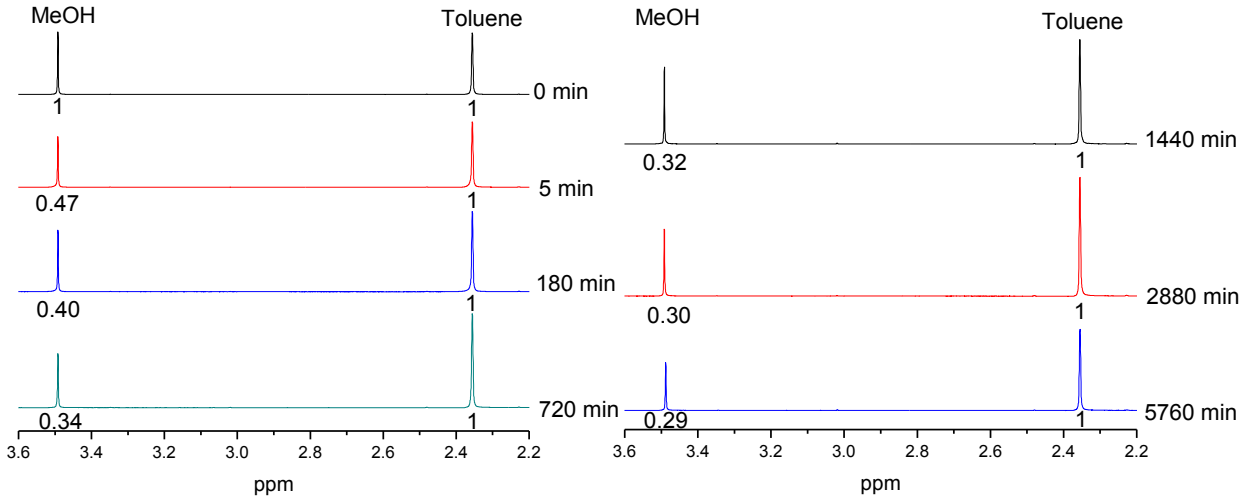

Fig. S18 ^{1}H-NMR spectra in CD_3Cl of aliquots taken at various adsorption times from suspensions containing initial amounts of MeOH (18 μL, 14.22mg, 0.444 mmol, 2 eq.), **UCY-**

5/dry (0.1 g, 0.222 mmol) and toluene (47 μL, 41.0 mg, 0.444 mmol) in 4mL CD_3Cl. The numbers under each peak represent the values of the peak integrals.

D. MeOH/EtOH selectivity experiments

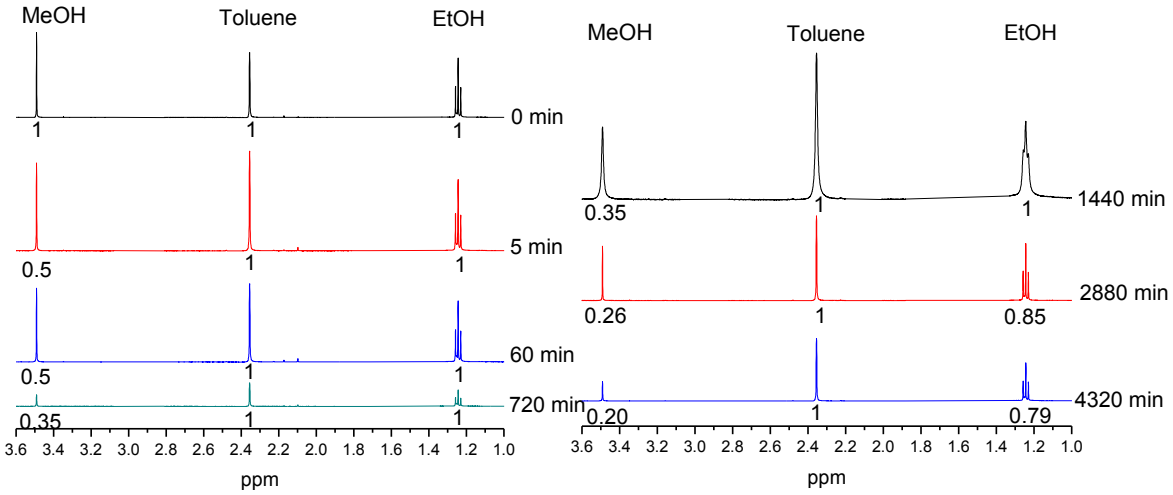

Fig. S19 ^{1}H-NMR spectra in CD_3Cl of aliquots taken at various adsorption times from suspensions containing equimolar initial amounts of MeOH (9 μL, 7.11 mg, 0.222 mmol, 1 eq.), EtOH (12.9 μL, 10.2 mg, 0.222 mmol, 1 eq.), toluene (23. 5 μL, 20.5mg, 0.222mmol), **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl. The numbers under each peak represent the values of the peak integrals.

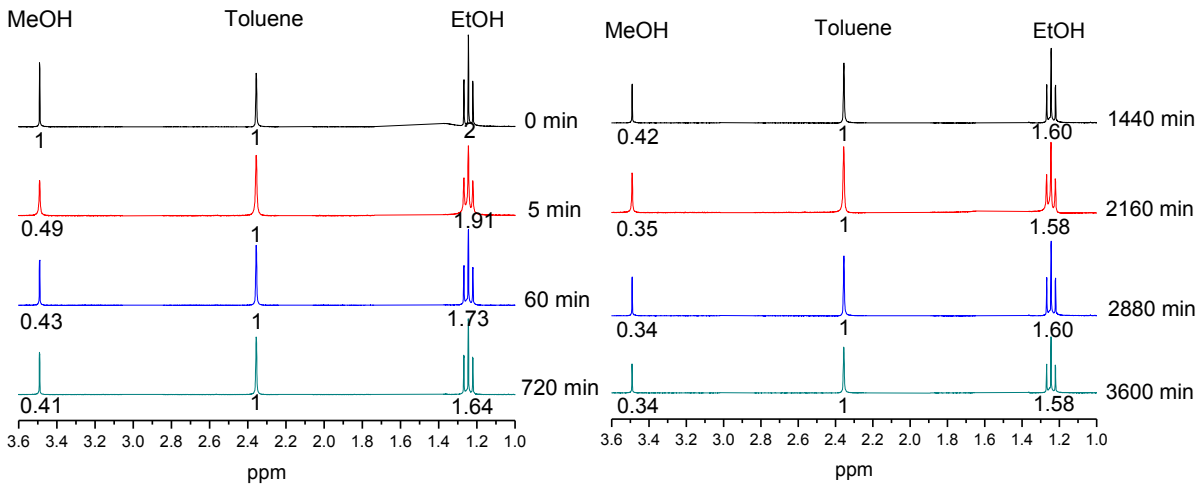

Fig. S20 ^{1}H-NMR spectra in CD_3Cl of aliquots taken at various adsorption times from suspensions containing initial amounts of MeOH (9μL, 7.11mg, 0.222mmol, 1 eq.), EtOH (25.8 μL, 20.4mg, 0.444mmol, 2 eq.), toluene (23. 5 μL, 20.5mg, 0.222mmol) and **UCY-5**/dry (0.1 g, 0.222 mmol) in 4mL CD_3Cl. The numbers under each peak represent the values of the peak integrals.