SUPPORTING INFORMATION

Insertion of Functional Groups into a Nd^{3+} Metal – Organic Framework via Single–Crystal–to–Single–Crystal Coordinating Solvent Exchange

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Elemental analyses

Anal. Calcd(%) for **H_3CIP**·2EtOH·H_2O: $C_{20}H_{25}NO_9$: C, 56.72; H, 5.95; N, 3.31. Found: C, 56.60; H, 5.85; N, 3.24.

Anal. Calcd(%) for **UCY-2**·2H_2O: $C_{20.2}H_{23}N_{2.4}NdO_{10}$: C, 40.33; H, 3.86; N, 5.59. Found: C, 40.24; H, 3.72; N, 5.51.

Anal. Calcd(%) for **UCY-2/** MeOH·H_2O: $C_{17}H_{16}NNdO_9$: C, 39.23; H, 3.10; N, 2.69. Found: C 39.35, H 3.05, N 2.60.

Anal. Calcd(%) for **UCY-2/** EtOH·1.5H_2O: $C_{20}H_{23}NNdO_{9.5}$: C, 42.03; H, 4.06; N, 2.45. Found: C, 42.10; H, 3.95; N, 2.50.

Anal. Calcd(%) for **UCY-2/** THF·2H_2O: $C_{20}H_{22}NNdO_{10}$: C, 41.52; H, 3.84; N, 2.42. Found: C, 41.60; H, 3.78; N, 2.47.

Anal. Calcd(%) for **UCY-2/** Acetone·H_2O: $C_{22}H_{22}NNdO_9$: C, 45.05; H, 3.78; N, 2.38. Found: C, 45.12; H, 3.68; N, 2.44.

Anal. Calcd(%) for **UCY-2/** py·3py·H_2O: $C_{57}H_{47}N_7Nd_2O_{15}$: C, 50.55; H, 3.50; N, 7.24. Found: C, 50.48; H, 3.56; N, 7.30.

Anal. Calcd(%) for **UCY-2/** merpdH_2·H_2O: $C_{22}H_{26}NNdO_{11}S_2$: C, 38.48; H, 3.82; N, 2.04; S, 9.32. Found: C, 38.52; H, 3.91; N, 2.10; S, 9.40.

Anal. Calcd(%) for **UCY-2/** BME·2H_2O: $C_{17.3}H_{18.6}NNdO_{10}S_{0.65}$: C, 36.87; H, 3.33; N, 2.49; S 3.69. Found: C, 36.91; H, 3.40; N, 2.37; S, 3.58.

Anal. Calcd(%) for **UCY-2/** 2hpH_2·3H_2O: $C_{26}H_{29}N_2NdO_{12}$: C, 44.38; H, 4.16; N, 3.98. Found: C, 44.42; H, 4.05; N, 4.13.

Anal. Calcd(%) for **UCY-2/** Im·1.5H_2O: $C_{22}H_{19}N_5NdO_{7.5}$: C, 42.92; H, 3.11; N, 11.38. Found: C, 43.03; H, 3.22; N, 11.45.

Anal. Calcd(%) for **UCY-2/** atzH·2H_2O: $C_{18}H_{18}N_5NdO_9$: C, 36.61; H, 3.07; N, 11.87. Found: C, 36.71; H, 3.16; N, 11.96.

Anal. Calcd(%) for **UCY-2/** Cl·ImH·H_2O: $C_{35}H_{25}ClN_4Nd_2O_{14}$: C, 40.23; H, 2.41; N, 5.37. Found: C, 40.15; H, 2.37; N, 5.44.

Anal. Calcd(%) for **UCY-2/** mIma·2H_2O: $C_{21}H_{18}N_3NdO_9$: C, 42.14; H, 3.03; N, 7.02. Found: C, 42.21; H, 3.14; N, 6.98.

Anal. Calcd(%) for **UCY-2/** Im-atzH·atzH·H_2O: $C_{21}H_{20}N_7NdO_8$: C, 39.37; H, 3.15; N, 15.32. Found: C, 39.42; H, 3.10; N 15.41.

Table S1. Selected crystal data for H_3CIP, **UCY-2** and exchanged compounds.

Compound	H_3CIP	**UCY-2**	/MeOH	/EtOH	/acetone	/THF	/py
Chemical formula	$C_{40}H_{46}N_2O_{16}$	$C_{20\cdot20}H_{16\cdot40}N_{2\cdot40}NdO_8$	$C_{17}H_{11}NNdO_9$	$C_{20}H_{18}NNdO_8$	$C_{22}H_{20}NNdO_8$	$C_{24}H_{24}NNdO_9$	$C_{57}H_{41}N_7Nd_2O_{14}$
Formula Mass	810.79	565.00	517.51	544.59	570.63	614.68	1336.45
a/A	3.8349(4)	28.894(2)	28.483(3)	28.660(2)	28.618 (2)	28.832 (2)	13.682 (2)
b/A	16.575 (2)	14.273(2)	14.523(2)	14.8265(9)	14.465(2)	14.377(2)	15.001 (2)
c/Å	30.154(2)	13.645(2)	12.300(2)	12.6284(9)	12.827(2)	13.247 (2)	15.649(2)
α/°	91.716(6)	90.00	90.00	90.00	90.00	90.00	95.751(9)
β/°	93.400(7)	100.06(2)	106.76(2)	103.357(5)	103.661(7)	100.622(7)	113.163(9)
γ/°	94.285(8)	90.00	90.00	90.00	90.00	90.00	90.493(9)
V/Å^3	1906.9(3)	5541(2)	4871.9(9)	5221.1(5)	5159.7(6)	5397.1(6)	2934.2(5)
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*P*1	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*P*$\bar{1}$
Z	2	8	8	8	8	8	2
Radiation type	CuKα	MoKα	CuKα	MoKα	MoKα	MoKα	MoKα
μ/mm^{-1}	0.927	1.913	16.625	2.026	2.054	1.972	1.818
Total reflections	9328	13820	7995	11049	12195	10210	22538
Independent reflections	5633	4869	4290	4591	4541	4741	10315
R_{int}	0.0381	0.0581	0.0417	0.0407	0.0539	0.0454	0.0578
Final R_1 values ($I > 2\sigma(I)$)	0.0887	0.0594	0.0578	0.0475	0.0484	0.0448	0.0500
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2468	0.1640	0.1548	0.1350	0.1403	0.1180	0.1175
Final R_1 values (all data)	0.1126	0.0771	0.0749	0.0620	0.0633	0.0608	0.0743
Final $wR(F^2)$ values (all data)	0.2568	0.1768	0.1664	0.1435	0.1495	0.1255	0.1276
Goodness of fit on F^2	1.120	1.039	1.058	1.018	1.080	1.096	0.998

Table S2. Selected crystal data for exchanged compounds.

Compound	/merpdH$_2$	/BME	/Im	/2hpH$_2$	/atzH	mIma	/Cl	/im-atzH
Chemical formula	$C_{22}H_{20}NNdO_{10}S_2$	$C_{17\cdot30}H_{10\cdot60}NNdO_8S_{0\cdot65}$	$C_{22}H_{14}N_5NdO_6$	$C_{26}H_{22}N_2NdO_9$	$C_{18}H_{10}N_5NdO_7$	$C_{21}H_{14}N_3NdO_7$	$C_{35}H_{19}ClN_4Nd_2O_{15}$	$C_{21}H_{12}N_7NdO_8$
Formula Mass	666.75	525.55	588.62	650.70	552.55	564.59	1059.47	634.62
a/Å	29.1676(2)	28.5413(7)	28.618(2)	28.2238(8)	28.927(2)	29.042(2)	28.534(2)	29.846(2)
b/Å	14.4488(6)	14.9992(4)	14.0687(6)	15.1581(5)	13.8282(7)	13.7951(6)	14.7711(8)	12.5843(5)
c/Å	13.0926(5)	13.2796(5)	13.2796(7)	13.5868(5)	13.165(2)	13.0814(6)	13.6945(9)	14.1180(5)
α/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β/°	98.748(4)	100.320(3)	102.717(5)	100.014(3)	102.340(7)	100.785(4)	98.997(7)	95.627(3)
γ/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	5453.5(3)	5593.0(3)	5215.4(4)	5724.1(3)	5144.7(6)	5148.4(4)	5700.8(6)	5277.0(3)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
Z	8	8	8	8	8	8	4	8
Radiation type	MoKα	MoKα	MoKα	MoKα	CuKα	MoKα	MoKα	MoKα
μ/mm^{-1}	2.109	1.935	2.033	1.857	15.771	2.057	1.899	2.023
Total reflections	12096	11355	11464	14117	8871	11278	11380	13298
Independent reflections	4795	4919	4574	5044	4714	4535	4986	4619
R_{int}	0.1177	0.0342	0.0381	0.0415	0.0305	0.0387	0.0572	0.0583
Final R_1 values ($I > 2\sigma(I)$)	0.0531	0.0440	0.0476	0.0406	0.0404	0.0531	0.0576	0.0454
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1423	0.1378	0.1285	0.1128	0.1067	0.1472	0.1634	0.1292
Final R_1 values (all data)	0.0698	0.0573	0.0611	0.0523	0.0513	0.0688	0.0752	0.0551
Final $wR(F^2)$ values (all data)	0.1531	0.1477	0.1358	0.1180	0.1123	0.1539	0.1736	0.1365
Goodness of fit on F^2	1.023	1.073	1.102	1.088	1.119	1.065	1.087	1.084

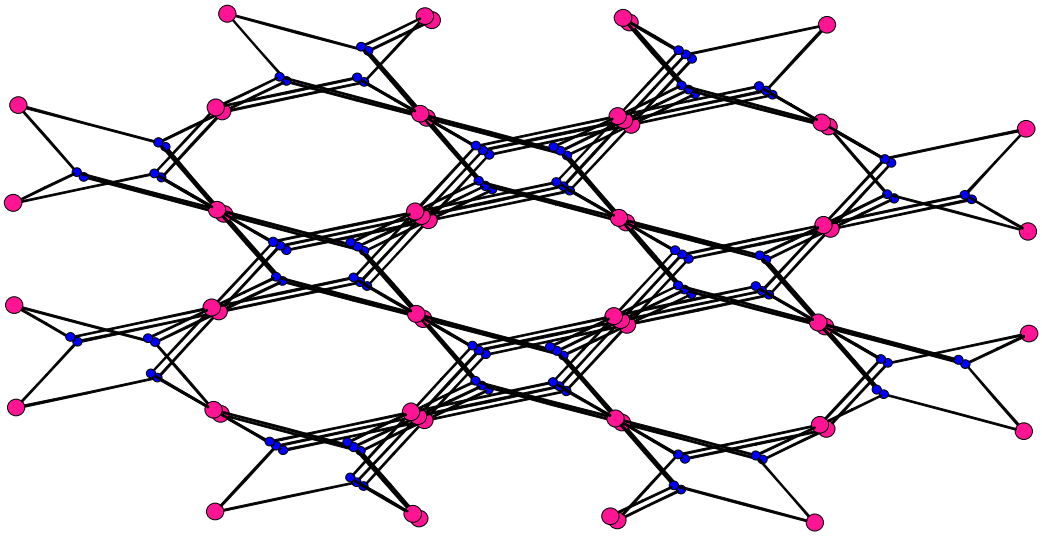

Figure S1. Representation of the flu-3,6-C2/c topology of **UCY-2**. Pink and blue spheres represent the 6-c and 3-c nodes, respectively.

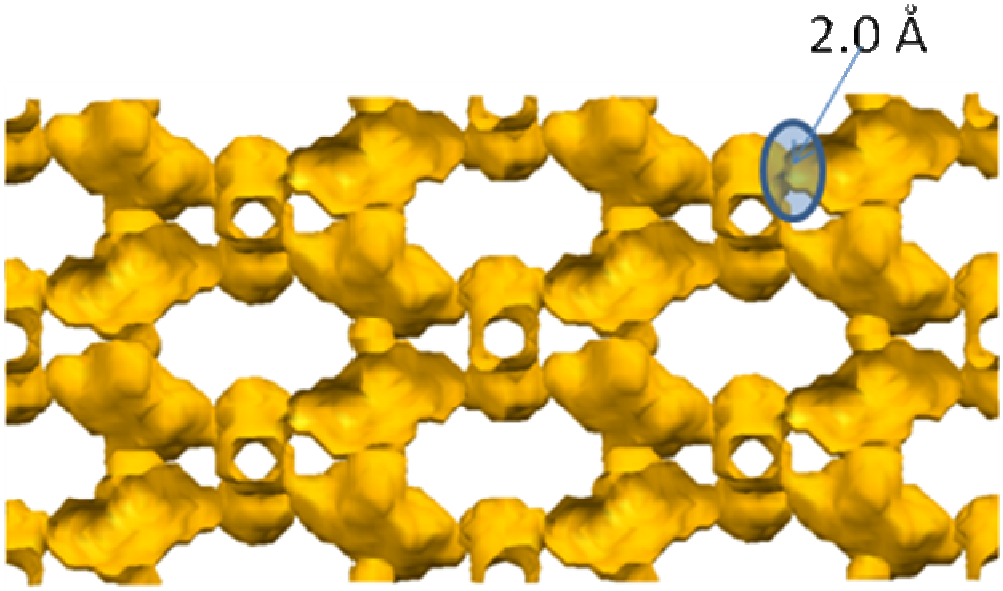

Figure S2. Representation of the pore network of **UCY-2**. The passages connecting the pores of **UCY-2** are ~ 2 Å wide as can be calculated with MERCURY.

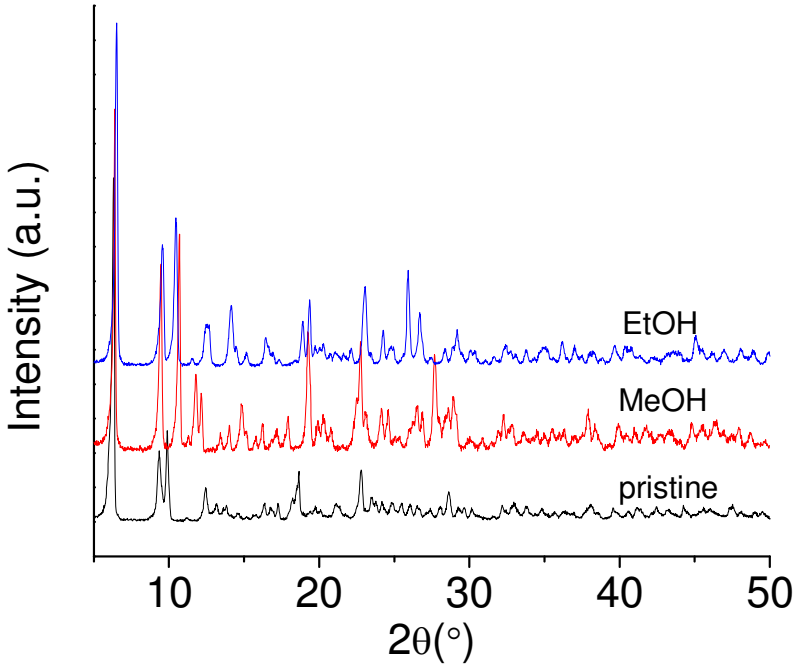

Figure S3. PXRD patterns of **UCY-2** and alcohol-exchanged products.

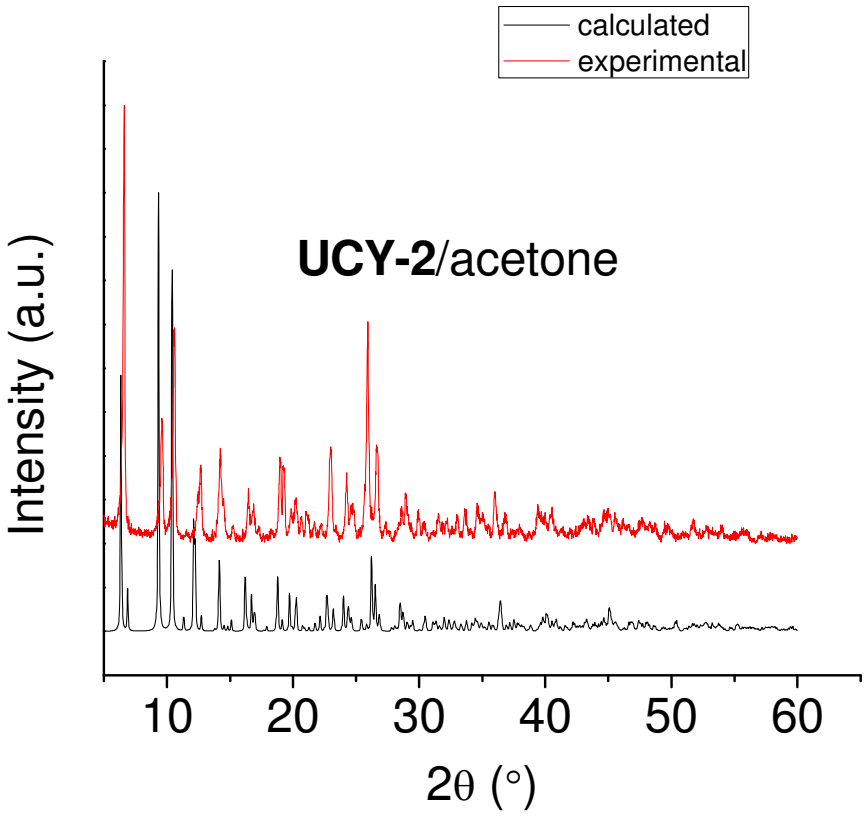

Figure S4. Experimental and calculated (from the crystal structure) PXRD patterns of **UCY-2**/acetone.

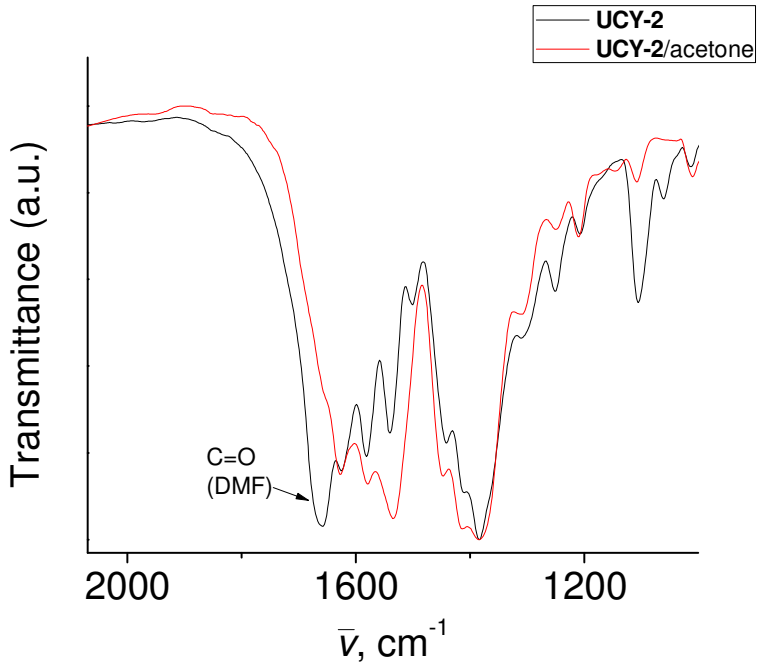

Figure S5. IR spectra of **UCY-2** and **UCY-2/**acetone. The spectrum of **UCY-2/**acetone does not contain the characteristic band of DMF (C=O bond) at 1660 cm^{-1} existing in the spectrum of **UCY-2**.

Figure S6. Photos of the crystals of **UCY-2**, **UCY-2/**merpdH$_2$ and **UCY-2/**acetone.

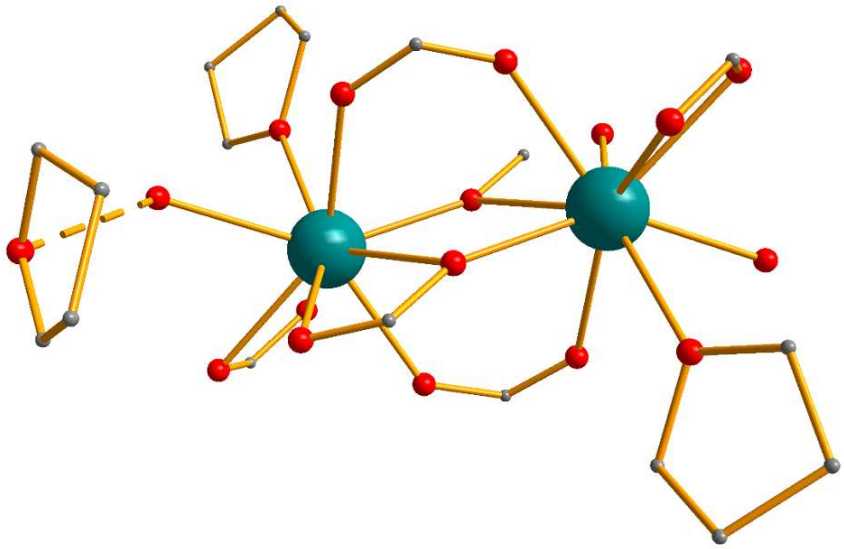

Figure S7. Representation of the SBU of **UCY-2/**THF emphasizing on the hydrogen bonds (dashed lines) formed between guest THF molecules and terminal water ligands.

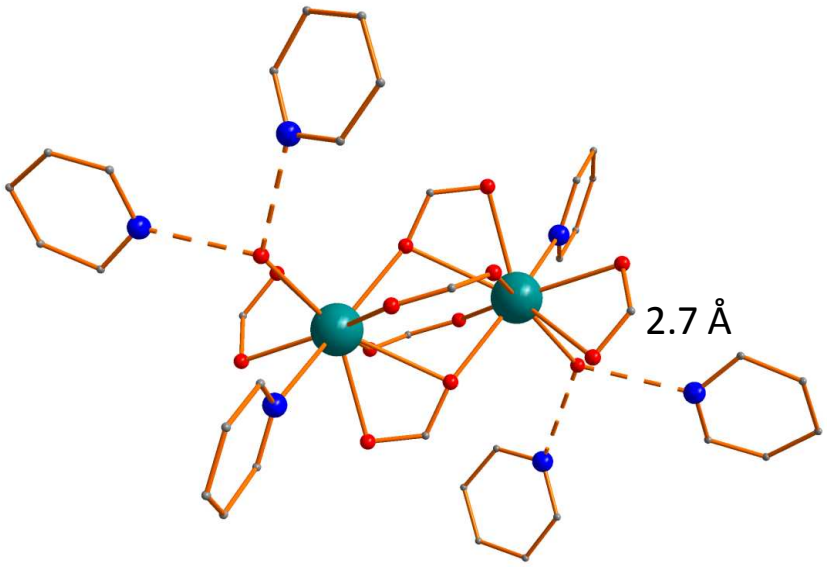

Figure S8. Representation of the SBU of **UCY-2/**py emphasizing on the hydrogen bonds (dashed lines) formed between guest py molecules and terminal water ligands.

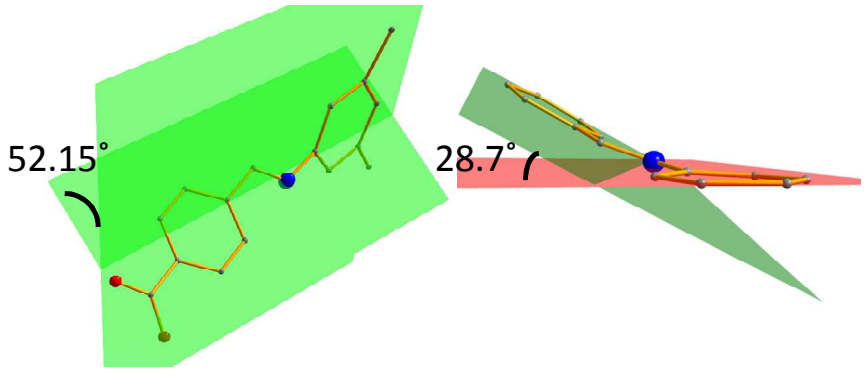

Figure S9. The dihedral angles between the planes of the phenyl rings of CIP^{3-} ligands in **UCY-2**/py.

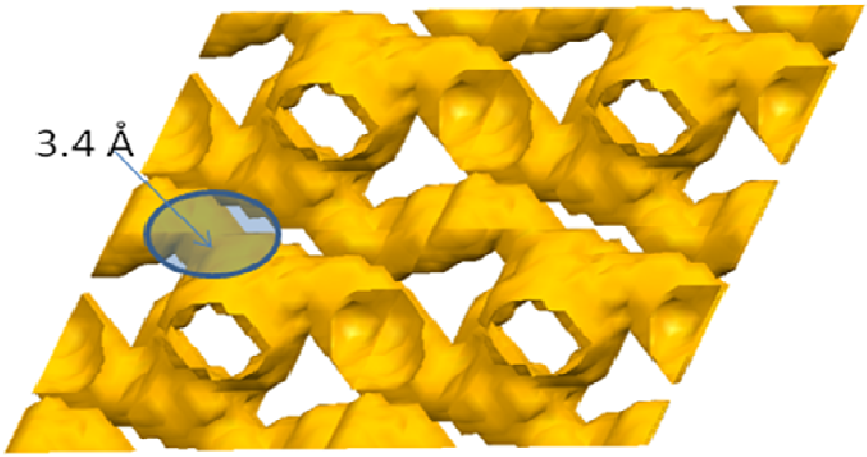

Figure S10. Representation of the pore network of **UCY-2**/py. The passages connecting the pores of **UCY-2**/py are ~ 3.4 Å wide as was calculated using program MERCURY.

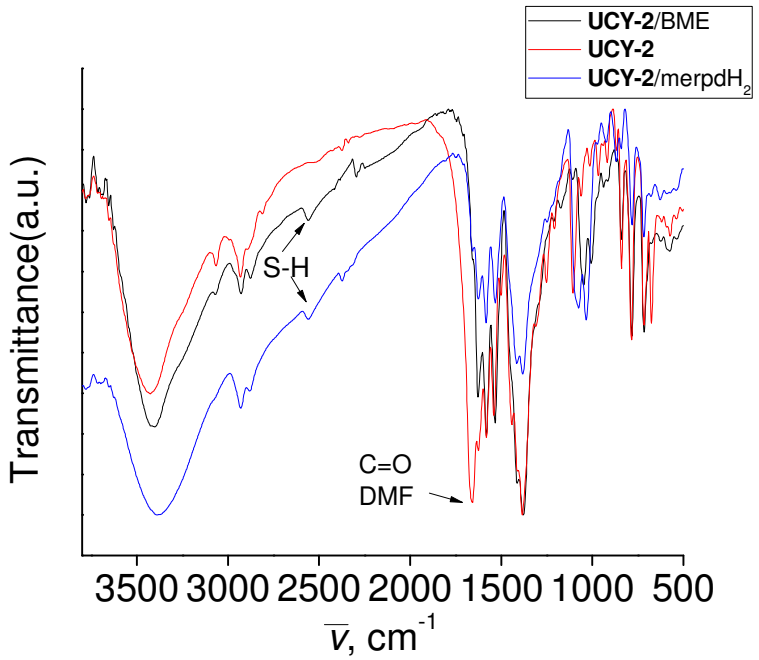

Figure S11. IR-spectra of **UCY-2**, **UCY-2**/BME and **UCY-2**/merpdH_2. The spectra of the last two materials display the characteristic peak of S-H at 2560 cm^{-1} and do not contain the peak of DMF(1660 cm^{-1}) existing in the spectrum of pristine **UCY-2**.