Electronic Supplementary Information

Immobilization of Co-containing Polyoxometalates in MIL-101(Cr): Structural Integrity versus Chemical Transformation

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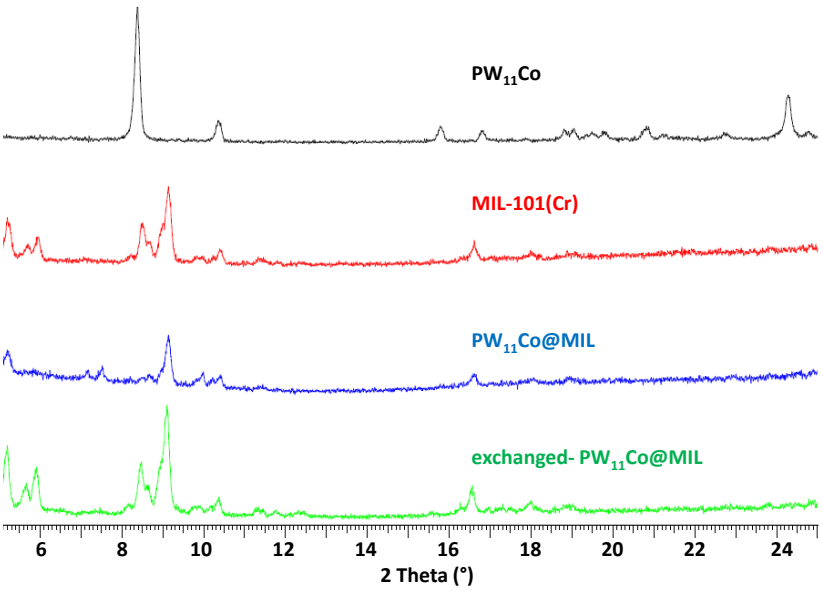
Synthesis of MILI-101(Cr):

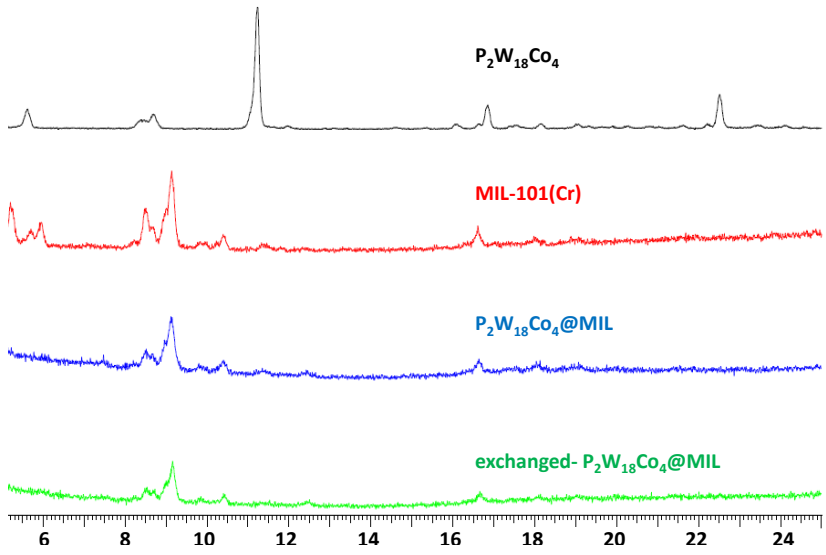
A mixture of $Cr(NO_3).9H_2O$ (2 g, 5 mmol), 1,4-benzene-dicarboxylic acid (terephtalic acid, 1.4 g, 8.4 mmol) and 25 mL of distilled water was added in a Teflon container inside an autoclave. Then the autoclave was heated for 9 h at 493 K in an oven under static conditions. Once the synthesis was completed, the solid product was filtered off using a glass filter with a pore size between 40 and 100 μm to remove free terephthalic acid. Then the solid product was washed with water several times, dried with ethanol and diethyl ether. The activation of the MIL-101(Cr) (extraction of the terephthalic acid encapsulated into the pores) was performed thanks to a soxhlet extractor with ethanol under reflux conditions as described for MIL-101NH_2(Al). Yield: 53% (based on Cr). Elemental analysis is in agreement with the following formula $[Cr^{III}_3(H_2O)_3O(O_2CC_6H_4CO_2)_3]NO_3 \cdot 2EtOH$. Anal. Calcd (Found) for $Cr_3H_{30}O_{21}C_{28}N$: C 38.54 (38.50), H 3.45 (3.39), N 1.60 (1.44). The solvent molecules are removed by standing in water before drying the solid in an oven at 393 K overnight before the impregnation experiments.

1. M. Hartmann, and M. Fischer, *Microporous Mesoporous Mater.*, 2012, **164**, 38.

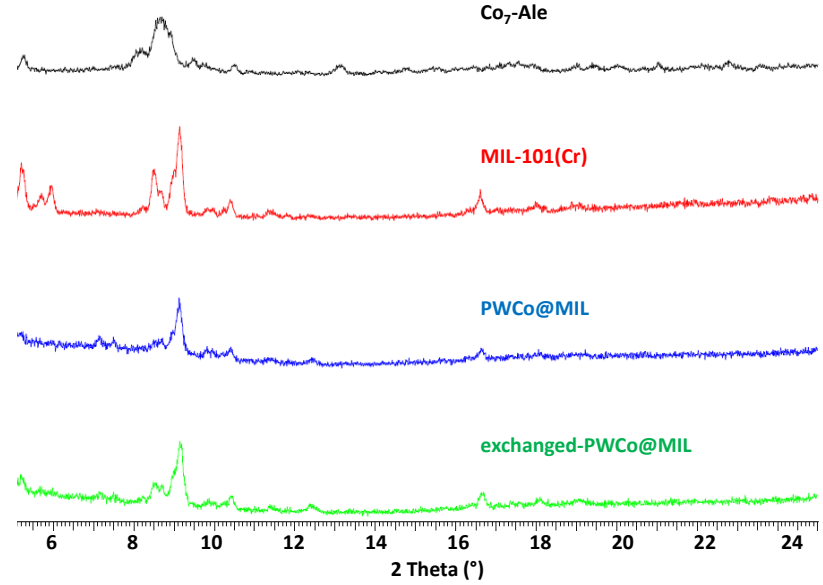
Figure S1. X-Ray diffraction patterns of the POM precursor, MIL-101(Cr), POM@MIL and POM@MIL after exchange with LiCl for a) $PW_{11}Co$, b) $P_2W_{18}Co_4$ and c) Co_7-Ale POM.



a)

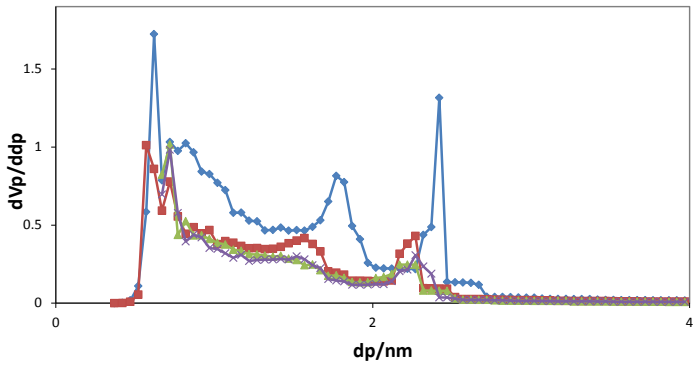


b)

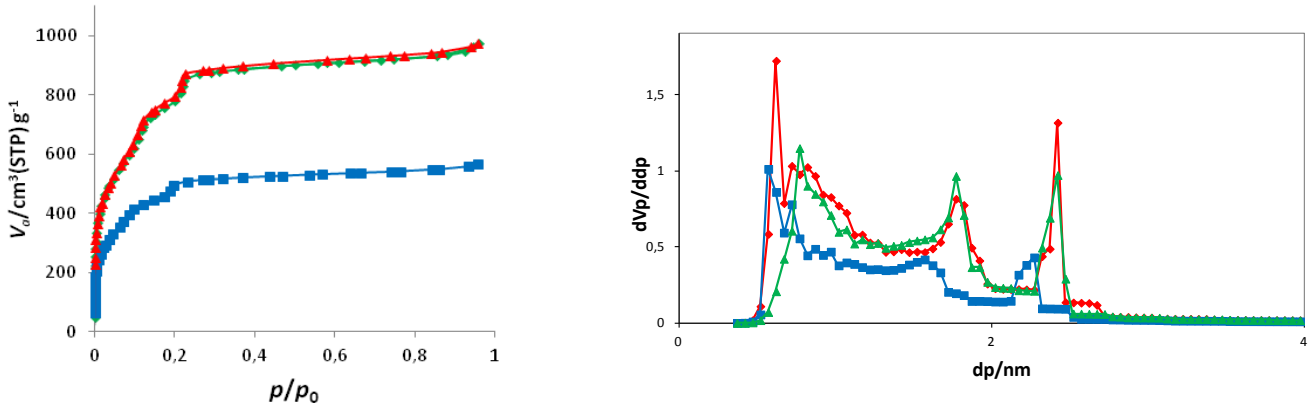


c)

Fig. S2 A) Porous distribution by Horvath-Kawazoe method of MIl-101(Cr) (blue), $PW_{11}Co$@MIL (red), $P_2W_{18}Co_4$@MIL (green) and PWCo@MIL (purple).



B) N_2 adsorption/desorption isotherm (left) and porous distribution (right) of MIl-101(Cr) (red), $PW_{11}Co$@MIL (blue) and exchanged-$PW_{11}Co$@MIL (green).



C) N_2 adsorption/desorption isotherm (left) and porous distribution (right) of MIl-101(Cr) (red), $P_2W_{18}Co_4$@MIL (blue) and exchanged-$P_2W_{18}Co_4$@MIL (green).

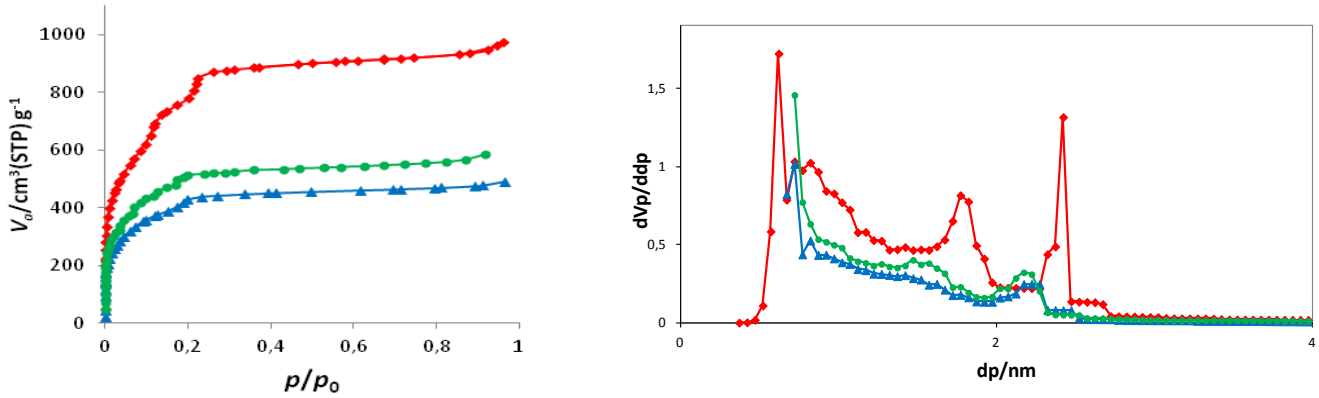


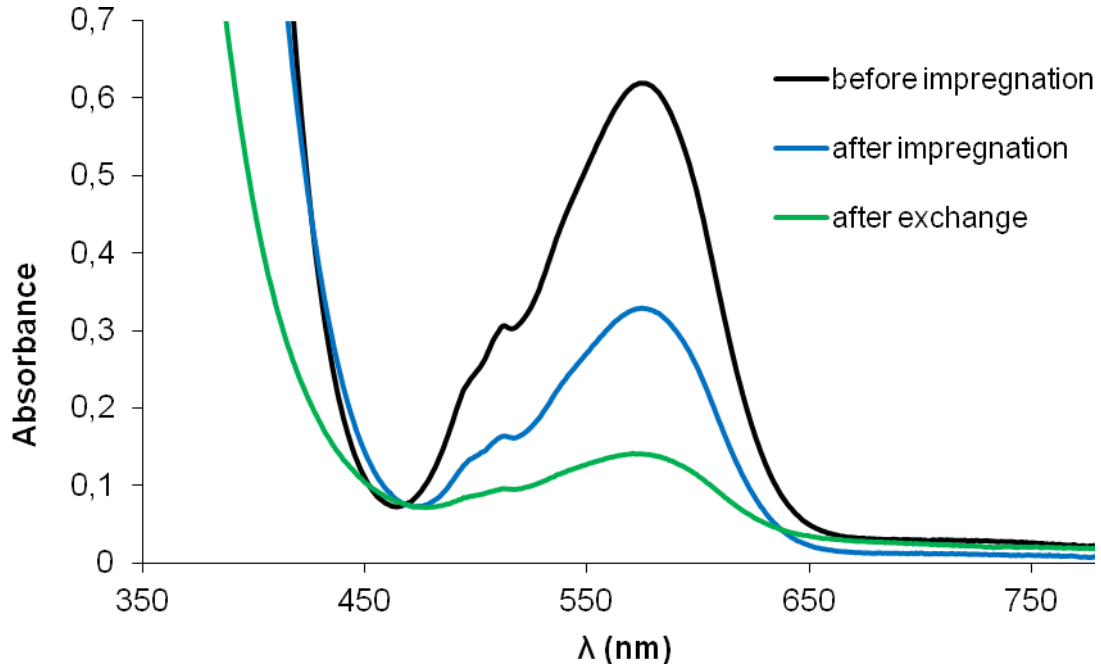
Table S1. Specific surface area, total pore volume and maxima for pore size distribution.

	Big cavity d(nm)	Small cavity d(nm)	S BET ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)
MIL-101(Cr)	**2.42**	**1.77**	**3007**	**1.507**
$PW_{11}Co$@MIL	**2.27**	**1.57**	**1785**	**0.873**
exchanged-$PW_{11}Co$@MIL	**2.42**	**1.77**	**3047**	**1.504**
$P_2W_{18}Co4$@MIL	**2.22**	**~ 1.5**	**1534**	**0.760**
exchanged-$P_2W_{18}Co_4$@MIL	**2.17**	**1.57**	**1823**	**0.904**
PWCo@MIL	**2.27**	**1.52**	**1432**	**0.704**

Table S2. Semi-quantitative EDX analysis ; the reported experimental ratios result from an average of 5 to 10 measurements.

	W/P	W/Co	W/Cr	Cl/Cr
Experimental values for $PW_{11}Co$@MIL	13.2	14.5	0.72	-
Calc. value for $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][PW_{11}O_{39}Co(H_2O)]_{0.2}$	11	11	0.73	-
Experimental values for exchanged-$PW_{11}Co$@MIL	10.1	14.4	0.03	0.38
Calc. value for $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][PW_{11}O_{39}Co(H_2O)]_{0.01}Cl_{0.95}$	11	11	0.03	0.32
Experimental values for $P_2W_{18}Co_4$@MIL	8.2	5.3	0.72	-
Calc. value for $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][P_2W_{18}O_{68}Co_4(H_2O)_2]_{0.1}$	9	4.5	0.60	-
Experimental values for exchanged-$P_2W_{18}Co_4$@MIL	9.7	5.7	0.48	0.07
Calc. value for $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][P_2W_{18}O_{68}Co_4(H_2O)_2]_{0.08}Cl_{0.2}$	9	4.5	0.48	0.07
Experimental values for PWCo@MIL	2.9	5.4	0.65	-
Calc. value for $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][P_2W_{18}O_{68}Co_7(OH)_2(H_2O)_4(O_3PC(O)(C_3H_6N_3)PO_3)_2]_{0.07}$	3	2.6	0.42	-
Experimental values for exchanged-PWCo@MIL	2.0	4.8	0.41	0.08

Figure S3. a) UV-vis spectra of a solution of $P_2W_{18}Co_4$, same solution 24 h after addition of MIL-101(Cr) and the solution obtained by exchange of $P_2W_{18}Co_4$@MIL with LiCl.

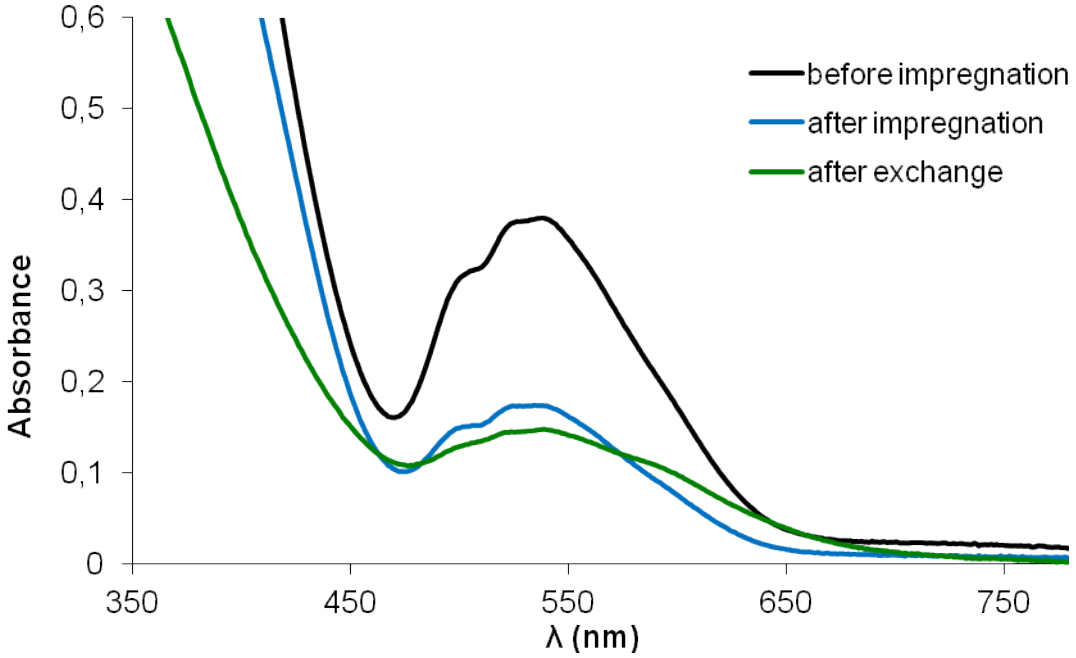


	λ / nm	A	c / mol l^{-1}	V / mL	n / mol
Solution of $P_2W_{18}Co_4$ before impregnation	574	0.619	$3.64\ 10^{-3}$	17.5	$6.34\ 10^{-5}$
Solution of $P_2W_{18}Co_4$ after impregnation	574	0.329	$1.93\ 10^{-3}$	17.5	$3.36\ 10^{-5}$
Solution of $P_2W_{18}Co_4$@MIL after extraction	574	0.142	$0.83\ 10^{-3}$	3	$2.50\ 10^{-6}$

For the impregnation experiment $K_{10}P_2W_{18}Co_4$ (0.350 g, $6.34\ 10^{-5}$ mol) was dissolved in 17.5 mL of water before addition of MIL-101(Cr) (0.219 g, $2.80\ 10^{-4}$ mol). From the table above we can deduce that $2.98\ 10^{-5}$ mol of POM have been encapsulated for $2.80\ 10^{-4}$ mol of MIL, that gives a ratio POM/MIL = 0.1 consistent with the formula $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][P_2W_{18}O_{68}Co_4(H_2O)_2]_{0.1}$.

For the extraction experiment a suspension of $P_2W_{18}Co_4$@MIL (0.150 g) in 3 mL of 5 M LiCl was stirred for 24 h at room temperature. This sample of $P_2W_{18}Co_4$@MIL contains $1.24\ 10^{-5}$ mol of POM encapsulated. The results deduced from the UV-vis spectra thus indicate that 20% of the POM has been extracted.

Figure S4. a) UV-vis spectra of a solution of $PW_{11}Co$, same solution 24 h after addition of MIL-101(Cr) and the solution obtained by exchange of $PW_{11}Co$@MIL with LiCl.

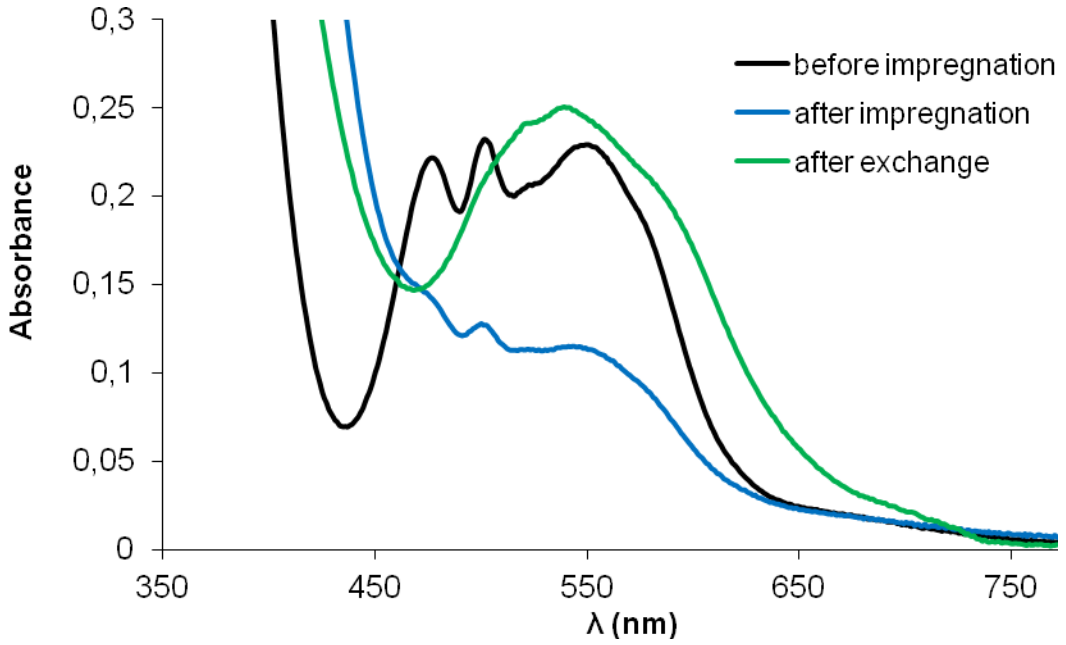


	λ / nm	A	c / mol l^{-1}	V / mL	n / mol
Solution of $PW_{11}Co$ before impregnation	538	0.381	$5.61\ 10^{-3}$	20	$1.12\ 10^{-4}$
Solution of $PW_{11}Co$ after impregnation	538	0.174	$2.56\ 10^{-3}$	20	$5.12\ 10^{-5}$
Solution of $PW_{11}Co$@MIL after extraction	538	0.149	$2.19\ 10^{-3}$	10	$2.19\ 10^{-5}$

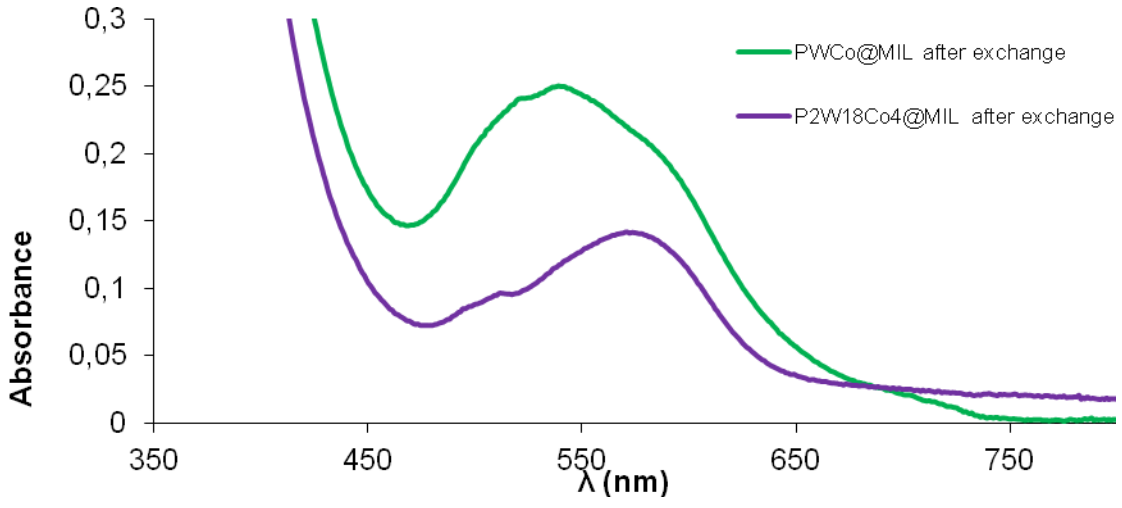
For the impregnation experiment $Cs_5PW_{11}Co$ (0.400 g, $1.12\ 10^{-4}$ mol) was dissolved in 20 mL of water before addition of MIL-101(Cr) (0.250 g, $3.20\ 10^{-4}$ mol). From the table above we can deduce that $6.08\ 10^{-5}$ mol of POM have been encapsulated for $3.20\ 10^{-4}$ mol of MIL, that gives a ratio POM/MIL = 0.19 consistent with the formula $[Cr_3(H_2O)_3O(O_2CC_6H_4CO_2)_3][PW_{11}O_{39}Co(H_2O)]_{0.2}$.

For the extraction experiment a suspension of $PW_{11}Co$@MIL (0.250 g) in 10 mL of 5 M LiCl was stirred for 24 h at room temperature. This sample of $PW_{11}Co$@MIL contains $3.00\ 10^{-5}$ mol of POM encapsulated. The results deduced from the UV-vis spectra thus indicate that at least 73% of the POM has been extracted.

Figure S5. a) Visible spectra of a solution of Co_7-Ale, same solution 24h after addition of MIL-101(Cr) and the solution obtained by exchange of PWCo@MIL with LiCl; b) comparison of the spectra of the solution obtained after exchange of the POM from PWCo@MIL and $P_2W_{18}Co_4$@MIL.



a)



b)

For the impregnation experiment $Na_9(NH_4)_5[(PW_9O_{34})_2Co_7(OH)_2(H_2O)_4(O_3PC(O)(C_3H_6NH_3)PO_3)_2]\cdot 35H_2O$ (0.246 g, 3.84 10^{-5} mol) was dissolved in 15 mL of water before addition of MIL-101(Cr) (0.200 g, 2.56 10^{-4} mol). For the extraction experiment a suspension of PWCo@MIL (0.150 g) in 3 mL of 5M LiCl in D_2O was stirred for 24 h at room temperature.

Figure S6. Comparison of ^{31}P NMR spectra of an aqueous solution of $PW_{11}Co$ a) before and b) after impregnation.

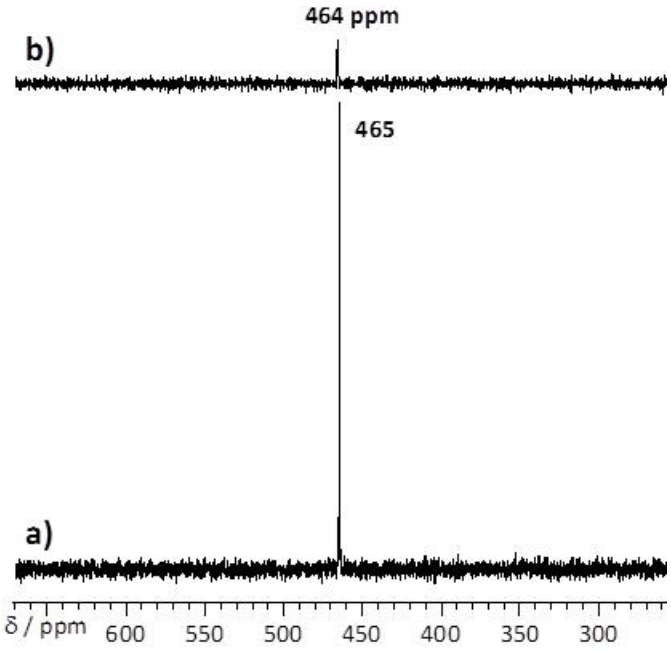
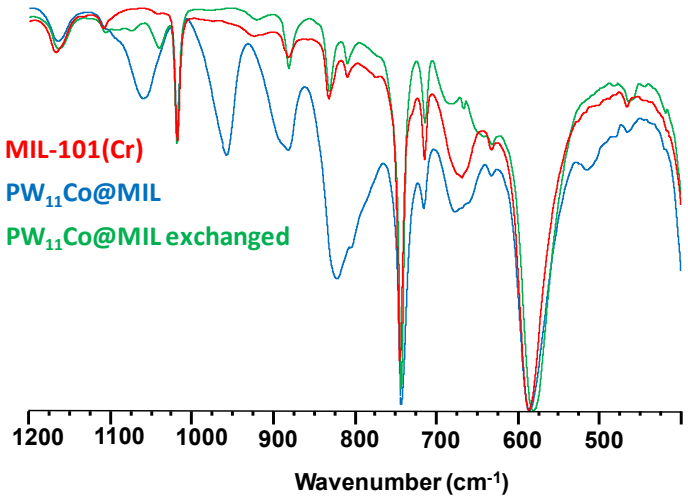
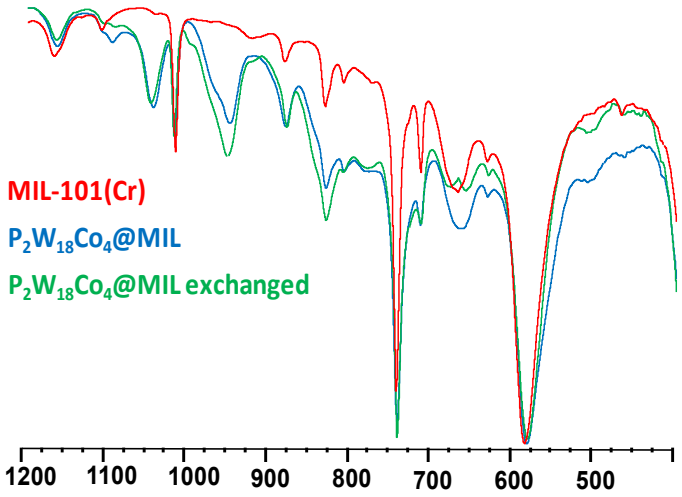


Figure S7. Infra-red spectra of MIL-101(Cr), POM@MIL and POM@MIL after exchange with LiCl for the a) $PW_{11}Co$, b) $P_2W_{18}Co_4$ and c) Co_7-Ale POM precursors.

a)



b)



c)