Effective detection of Ag^{+}, Hg^{2+} and dye adsorption properties studies of Ln-MOFs based on benzimidazole carboxylic acid ligand

Qing-Wei Cao, Tian-Cai Yue, Qing-Wei Dong, Qi-Chao Ma, Ze-Bei Xie, Duo-Zhi Wang* and Lu-Lu Wang*

State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, 830017, Xinjiang, P. R. China.

Supporting Information

Table S1 Crystallographic data and structure refinement details for **1-5**.

Complexes	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{30}H_{18}ClN_4O_8Pr$	$C_{30}H_{18}ClN_4O_8Nd$	$C_{30}H_{18}ClN_4O_8Eu$	$C_{30}H_{18}ClN_4O_8Ho$	$C_{30}H_{18}ClN_4O_8Ce$
Formula weight	1493.69	742.17	765.89	762.86	738.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*
Temperature/K	296(2)	296(2)	296(2)	296(2)	296(2)
a/Å	32.89(4)	33.038	33.009(4)	32.8110(18)	33.07(16)
b/Å	5.0867(6)	5.150	5.1593(7)	5.0340(3)	5.1931(3)
c/Å	16.067(2)	16.005	15.9530(19)	16.1817(9)	15.894(8)
a /deg	90	90	90	90	90
b /deg	90.82(4)	91.17	91.315(3)	90.401(2)	91.435(1)
g /deg	90	90	90	90	90
V/Å^3	2688.1(6)	2722.7	2716.1(6)	2670.8(3)	2729.2(2)
Z	2	4	4	4	4
ρ_{calc}g/cm^3	1.845	1.811	1.873	1.897	1.796
μ/mm^{-1}	1.977	2.067	2.475	3.126	1.828
F(000)	1480	1468	1512	1469	1460

Reflections collected	18950	4264	18236	54560	20189
Independent	2367	2389	2386	4104	2418
R^a/wR^b[$I>2\sigma(I)$]	0.0576/0.1424	0.0848/0.20995	0.0632/0.1743	0.0518/0.1244	0.0369/0.1038

$R^a = \Sigma(|F_0|-|F_C|)/\Sigma|F_0|$, $wR^b = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)^2]^{1/2}$

Table S2 Selected bond lengths [Å] and angles [°] for **1-5**

Ln-MOF 1

O(1)-Pr(1)	2.372(8)	O(5)#2-Pr(1)-O(1)	75.6(2)
O(1)-Pr(1)#4	2.595(8)	O(3)#2-Pr(1)-O(1)	83.0(3)
O(2)-Pr(1)	2.372(8)	O(4)#5-Pr(1)-O(1)	132.0(3)
O(2)-Pr(1)#4	2.584(8)	O(2)-Pr(1)-O(1)	54.8(2)
O(3)-Pr(1)#2	2.309(8)	O(4)#7-Pr(1)-O(1)	78.1(3)
O(3)-Pr(1)#3	2.348(8)	O(5)#2-Pr(1)-O(3)#8	45.19(18)
O(4)-Pr(1)#5	2.385(8)	O(3)#2-Pr(1)-O(3)#8	91.1(3)
O(4)-Pr(1)#6	2.322(8)	O(4)#5-Pr(1)-O(3)#8	149.5(3)
Pr(1)-O(5)#2	1.91(2)	O(2)-Pr(1)-O(3)#8	132.2(3)
Pr(1)-O(3)#2	2.309(8)	O(4)#7-Pr(1)-O(3)#8	87.9(3)
Pr(1)-O(4)#5	2.385(8)	O(1)-Pr(1)-O(3)#8	77.8(3)
Pr(1)-O(4)#7	2.322(8)	O(5)#2-Pr(1)-O(1)#4	70.16(19)
Pr(1)-O(3)#8	2.348(8)	O(3)#2-Pr(1)-O(1)#4	74.1(2)
Pr(1)-O(1)#4	2.594(8)	O(4)#5-Pr(1)-O(1)#4	72.7(3)
Pr(1)-O(2)#4	2.584(8)	O(2)-Pr(1)-O(1)#4	146.8(4)
O(3)#1-O(5)-Pr(1)#2	81.2(7)	O(4)#7-Pr(1)-O(1)#4	124.2(3)
O(3)-O(5)-Pr(1)#2	79.5(7)	O(1)-Pr(1)-O(1)#4	145.7(3)
O(3)#1-O(5)-Pr(1)#3	79.5(7)	O(3)#8-Pr(1)-O(1)#4	77.5(2)
O(3)-O(5)-Pr(1)#3	81.2(7)	O(5)#2-Pr(1)-O(2)#4	108.4(3)
O(5)-O(3)-Pr(1)#2	54.6(7)	O(3)#2-Pr(1)-O(2)#4	123.6(3)
O(5)-O(3)-Pr(1)#3	53.6(7)	O(4)#5-Pr(1)-O(2)#4	72.6(2)
O(5)#2-Pr(1)-O(3)#2	45.89(18)	O(2)-Pr(1)-O(2)#4	134.1(3)
O(5)#2-Pr(1)-O(4)#5	126.2(3)	O(4)#7-Pr(1)-O(2)#4	75.3(3)
O(3)#2-Pr(1)-O(4)#5	87.3(3)	O(1)-Pr(1)-O(2)#4	147.7(4)
O(5)#2-Pr(1)-O(2)	117.4(3)	O(3)#8-Pr(1)-O(2)#4	83.2(3)
O(3)#2-Pr(1)-O(2)	88.9(3)	O(1)#4-Pr(1)-O(2)#4	49.8(2)
O(4)#5-Pr(1)-O(2)	78.3(3)	O(3)#2-Pr(1)-O(4)#7	160.8(3)
O(5)#2-Pr(1)-O(4)#7	129.8(4)	O(4)#5-Pr(1)-O(4)#7	103.1(3)
O(2)-Pr(1)-O(4)#7	77.7(3)		

Ln-MOF 2

Nd(1)-O(4)	2.385(8)	O(4)#2-Nd(1)-O(2)#1	127.0(3)
Nd(1)-O(4)#2	2.385(8)	O(3)#3-Nd(1)-O(2)#1	77.6(3)
Nd(1)-O(3)#3	2.400(8)	O(3)#4-Nd(1)-O(2)#1	74.2(3)
Nd(1)-O(3)#4	2.400(8)	O(4)-Nd(1)-O(2)#5	127.0(3)
Nd(1)-O(2)#1	2.526(8)	O(4)#2-Nd(1)-O(2)#5	87.7(3)
Nd(1)-O(2)#5	2.526(8)	O(3)#3-Nd(1)-O(2)#5	74.2(3)
Nd(1)-O(1)#5	2.530(7)	O(3)#4-Nd(1)-O(2)#5	77.6(3)
Nd(1)-O(1)#1	2.530(7)	O(2)#1-Nd(1)-O(2)#5	133.4(4)
Nd(1)-C(1)#1	2.878(12)	O(4)-Nd(1)-O(1)#5	75.9(3)
Nd(1)-C(1)#5	2.878(12)	O(4)#2-Nd(1)-O(1)#5	80.8(3)
O(1)-Nd(1)#1	2.530(7)	O(3)#3-Nd(1)-O(1)#5	74.7(3)
O(2)-Nd(1)#1	2.526(8)	O(3)#4-Nd(1)-O(1)#5	127.9(3)
O(3)-Nd(1)#6	2.400(8)	O(2)#1-Nd(1)-O(1)#5	148.1(3)
O(4)-Nd(1)-O(4)#2	89.6(4)	O(2)#5-Nd(1)-O(1)#5	51.4(3)
O(4)-Nd(1)-O(3)#3	88.1(3)	O(4)-Nd(1)-O(1)#1	80.8(3)
O(4)#2-Nd(1)-O(3)#3	155.2(3)	O(4)#2-Nd(1)-O(1)#1	75.9(3)
O(4)-Nd(1)-O(3)#4	155.2(3)	O(3)#3-Nd(1)-O(1)#1	127.9(3)
O(4)#2-Nd(1)-O(3)#4	88.1(3)	O(3)#4-Nd(1)-O(1)#1	74.7(3)
O(3)#3-Nd(1)-O(3)#4	104.0(4)	O(2)#1-Nd(1)-O(1)#1	51.4(3)
O(4)-Nd(1)-O(2)#1	87.7(3)	O(2)#5-Nd(1)-O(1)#1	148.1(3)
O(1)#5-Nd(1)-O(1)#1	146.9(4)		

Ln-MOF 3

Eu(1)-O(2)	2.383(6)	O(2)#1-Eu(1)-O(3)#2	126.7(2)
Eu(1)-O(2)#1	2.383(6)	O(1)#3-Eu(1)-O(3)#2	77.1(2)
Eu(1)-O(1)#3	2.422(6)	O(1)#4-Eu(1)-O(3)#2	74.7(2)
Eu(1)-O(1)#4	2.422(6)	O(5)-Eu(1)-O(3)#5	113.26(18)
Eu(1)-O(3)#2	2.528(7)	O(2)-Eu(1)-O(3)#5	126.7(2)
Eu(1)-O(3)#5	2.528(7)	O(2)#1-Eu(1)-O(3)#5	87.8(2)
Eu(1)-O(4)#5	2.540(7)	O(1)#3-Eu(1)-O(3)#5	74.7(2)
Eu(1)-O(4)#2	2.540(7)	O(1)#4-Eu(1)-O(3)#5	77.1(2)
O(1)-Eu(1)#6	2.422(6)	O(3)#2-Eu(1)-O(3)#5	133.5(4)
O(3)-Eu(1)#2	2.528(7)	O(5)-Eu(1)-O(4)#5	73.17(16)
O(4)-Eu(1)#2	2.540(7)	O(2)-Eu(1)-O(4)#5	75.7(2)
O(2)#1-O(5)-Eu(1)	83.2(4)	O(2)#1-Eu(1)-O(4)#5	80.6(2)
O(5)-Eu(1)-O(2)	44.95(16)	O(1)#3-Eu(1)-O(4)#5	75.6(2)
O(5)-Eu(1)-O(2)#1	44.95(16)	O(1)#4-Eu(1)-O(4)#5	127.3(2)
O(2)-Eu(1)-O(2)#1	89.9(3)	O(3)#2-Eu(1)-O(4)#5	148.5(2)
O(5)-Eu(1)-O(1)#3	128.02(17)	O(3)#5-Eu(1)-O(4)#5	51.4(2)

O(2)-Eu(1)-O(1)#3	87.6(2)	O(5)-Eu(1)-O(4)#2	73.17(16)
O(2)#1-Eu(1)-O(1)#3	155.9(2)	O(2)-Eu(1)-O(4)#2	80.6(2)
O(5)-Eu(1)-O(1)#4	128.02(17)	O(2)#1-Eu(1)-O(4)#2	75.7(2)
O(2)-Eu(1)-O(1)#4	155.9(2)	O(1)#3-Eu(1)-O(4)#2	127.3(2)
O(2)#1-Eu(1)-O(1)#4	87.6(2)	O(1)#4-Eu(1)-O(4)#2	75.6(2)
O(1)#3-Eu(1)-O(1)#4	104.0(3)	O(3)#2-Eu(1)-O(4)#2	51.4(2)
O(5)-Eu(1)-O(3)#2	113.26(18)	O(3)#5-Eu(1)-O(4)#2	148.5(2)
O(2)-Eu(1)-O(3)#2	87.8(2)	O(4)#5-Eu(1)-O(4)#2	146.3(3)

Ln-MOF 4

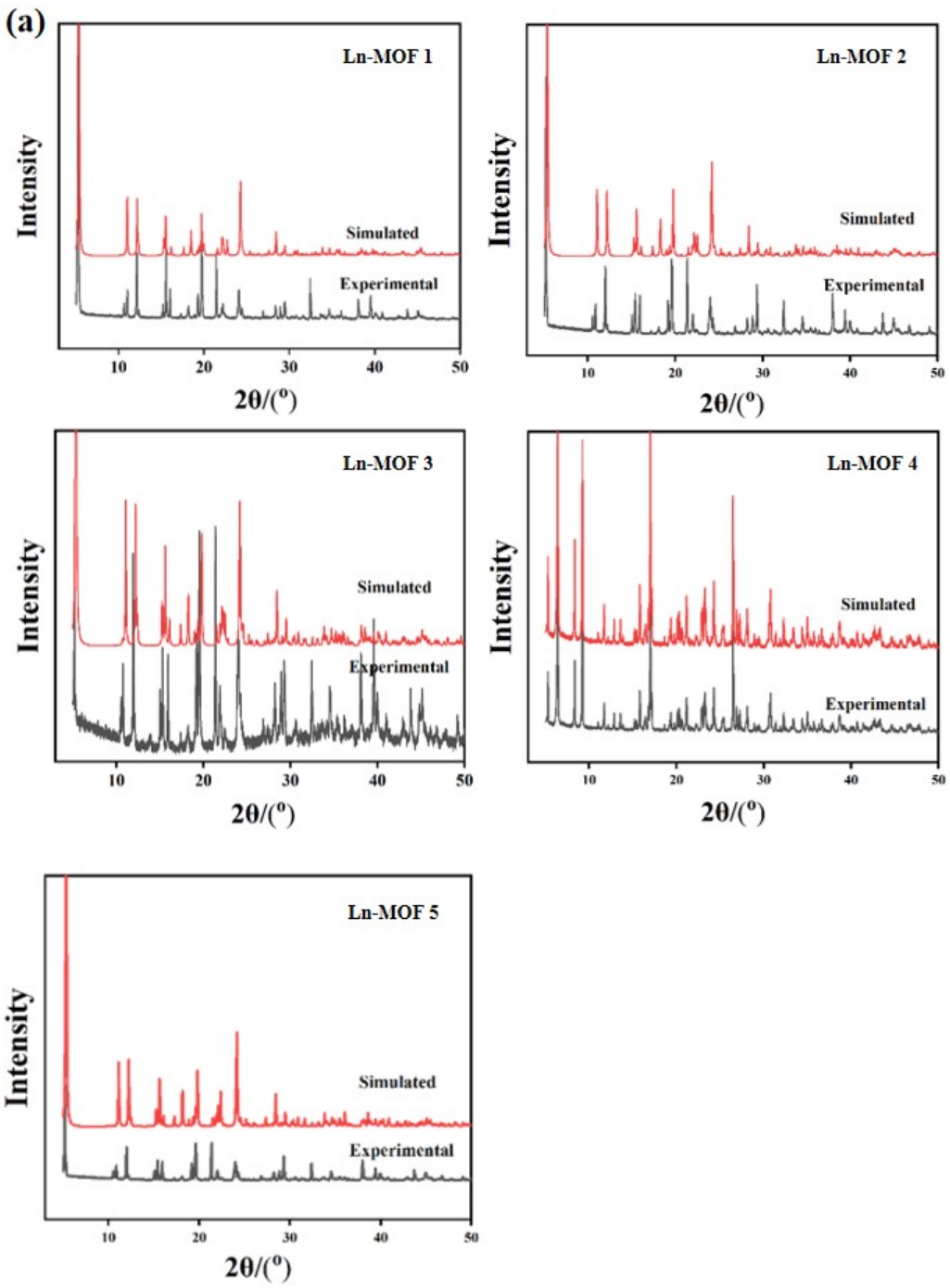
Ho(1)-O(2)#2	2.283(4)	O(1)#4-Ho(1)-O(4)#1	128.87(14)
Ho(1)-O(2)	2.283(4)	O(2)#2-Ho(1)-O(4)#5	80.17(14)
Ho(1)-O(1)#3	2.306(4)	O(2)-Ho(1)-O(4)#5	75.92(14)
Ho(1)-O(1)#4	2.306(4)	O(1)#3-Ho(1)-O(4)#5	128.87(14)
Ho(1)-O(4)#1	2.435(4)	O(1)#4-Ho(1)-O(4)#5	75.14(14)
Ho(1)-O(4)#5	2.435(4)	O(4)#1-Ho(1)-O(4)#5	145.5(2)
Ho(1)-O(3)#5	2.447(4)	O(2)#2-Ho(1)-O(3)#5	85.14(15)
Ho(1)-O(3)#1	2.447(4)	O(2)-Ho(1)-O(3)#5	128.53(13)
O(1)-Ho(1)#6	2.306(4)	O(1)#3-Ho(1)-O(3)#5	76.76(14)
O(3)-Ho(1)#1	2.447(4)	O(1)#4-Ho(1)-O(3)#5	75.34(15)
O(4)-Ho(1)#1	2.435(4)	O(4)#1-Ho(1)-O(3)#5	146.33(14)
O(2)#2-Ho(1)-O(2)	91.39(19)	O(4)#5-Ho(1)-O(3)#5	52.85(13)
O(2)#2-Ho(1)-O(1)#3	88.33(15)	O(2)#2-Ho(1)-O(3)#1	128.53(13)
O(2)-Ho(1)-O(1)#3	154.60(14)	O(2)-Ho(1)-O(3)#1	85.14(15)
O(2)#2-Ho(1)-O(1)#4	154.61(14)	O(1)#3-Ho(1)-O(3)#1	75.34(15)
O(2)-Ho(1)-O(1)#4	88.33(15)	O(1)#4-Ho(1)-O(3)#1	76.76(14)
O(1)#3-Ho(1)-O(1)#4	102.5(2)	O(4)#1-Ho(1)-O(3)#1	52.85(13)
O(2)#2-Ho(1)-O(4)#1	75.91(14)	O(4)#5-Ho(1)-O(3)#1	146.33(14)
O(2)-Ho(1)-O(4)#1	80.17(14)	O(3)#5-Ho(1)-O(3)#1	134.7(2)
O(1)#3-Ho(1)-O(4)#1	75.14(14)		

Ln-MOF 5

Ce(1)-O(2)#2	2.405(3)	O(1)#4-Ce(1)-O(3)#5	74.53(14)
Ce(1)-O(2)	2.405(3)	O(2)#2-Ce(1)-O(3)#1	126.30(12)
Ce(1)-O(1)#3	2.439(3)	O(2)-Ce(1)-O(3)#1	88.28(13)
Ce(1)-O(1)#4	2.439(4)	O(1)#3-Ce(1)-O(3)#1	74.53(13)
Ce(1)-O(3)#5	2.552(4)	O(1)#4-Ce(1)-O(3)#1	77.54(12)
Ce(1)-O(3)#1	2.552(4)	O(3)#5-Ce(1)-O(3)#1	133.55(19)
Ce(1)-O(4)#1	2.556(4)	O(2)#2-Ce(1)-O(4)#1	76.11(12)
Ce(1)-O(4)#5	2.556(4)	O(2)-Ce(1)-O(4)#1	81.08(12)

O(1)-Ce(1)#6	2.439(3)	O(1)#3-Ce(1)-O(4)#1	74.90(12)
O(3)-Ce(1)#1	2.552(4)	O(1)#4-Ce(1)-O(4)#1	126.85(12)
O(4)-Ce(1)#1	2.556(3)	O(3)#5-Ce(1)-O(4)#1	148.69(12)
O(2)#2-Ce(1)-O(2)	89.11(17)	O(3)#1-Ce(1)-O(4)#1	50.53(12)
O(2)#2-Ce(1)-O(1)#3	87.68(13)	O(2)#2-Ce(1)-O(4)#5	81.08(12)
O(2)-Ce(1)-O(1)#3	155.84(12)	O(2)-Ce(1)-O(4)#5	76.11(12)
O(2)#2-Ce(1)-O(1)#4	155.84(12)	O(1)#3-Ce(1)-O(4)#5	126.85(12)
O(2)-Ce(1)-O(1)#4	87.68(13)	O(1)#4-Ce(1)-O(4)#5	74.90(12)
O(1)#3-Ce(1)-O(1)#4	104.57(19)	O(3)#5-Ce(1)-O(4)#5	50.53(12)
O(2)#2-Ce(1)-O(3)#5	88.28(13)	O(3)#1-Ce(1)-O(4)#5	148.69(12)
O(2)-Ce(1)-O(3)#5	126.30(12)	O(4)#1-Ce(1)-O(4)#5	147.81(17)
O(1)#3-Ce(1)-O(3)#5	77.54(12)		

Symmetry codes, for 1: #1 -x+1,y,-z+3/2; #2 -x+1,-y,-z+1; #3 x,-y,z+1/2; #4 -x+1,y,-z+1/2; #5 -x+1,-y+1,-z+1; #6 x,-y+1,z+1/2; #7 x,-y+1,z-1/2; #8 x,-y,z-1/2; for 2: #1 -x+1,-y+2,-z+1; #2 -x+1,y,-z+1/2; #3 x,y+1,z; #4 -x+1,y+1,-z+1/2; #5 x,-y+2,z-1/2; #6 x,y-1,z; for 3: #1 -x+1,y,-z+1/2; #2 -x+1,-y+2,-z+1; #3 x,y+1,z; #4 -x+1,y+1,-z+1/2; #5 x,-y+2,z-1/2; #6 x,y-1,z; for 4: #1 -x+1,-y+2,-z+1; #2 -x+1,y,-z+3/2; #3 -x+1,y+1,-z+3/2; #4 x,y+1,z; #5 x,-y+2,z+1/2; #6 x,y-1,z; for 5: #1 -x+1,-y+2,-z+1; #2 -x+1,y,-z+3/2; #3 -x+1,y+1,-z+3/2; #4 x,y+1,z; #5 x,-y+2,z+1/2; #6 x,y-1,z.


(a)
Ln-MOF 1
Intensity
Simulated
Experimental
10
20
30
40
50
2θ/(°)
Ln-MOF 2
Intensity
Simulated
Experimental
10
20
30
40
50
2θ/(°)
Ln-MOF 3
Intensity
Simulated
Experimental
10
20
30
40
50
2θ/(°)
Ln-MOF 4
Intensity
Simulated
Experimental
10
20
30
40
50
2θ/(°)
Ln-MOF 5
Intensity
Simulated
Experimental
10
20
30
40
50
2θ/(°)

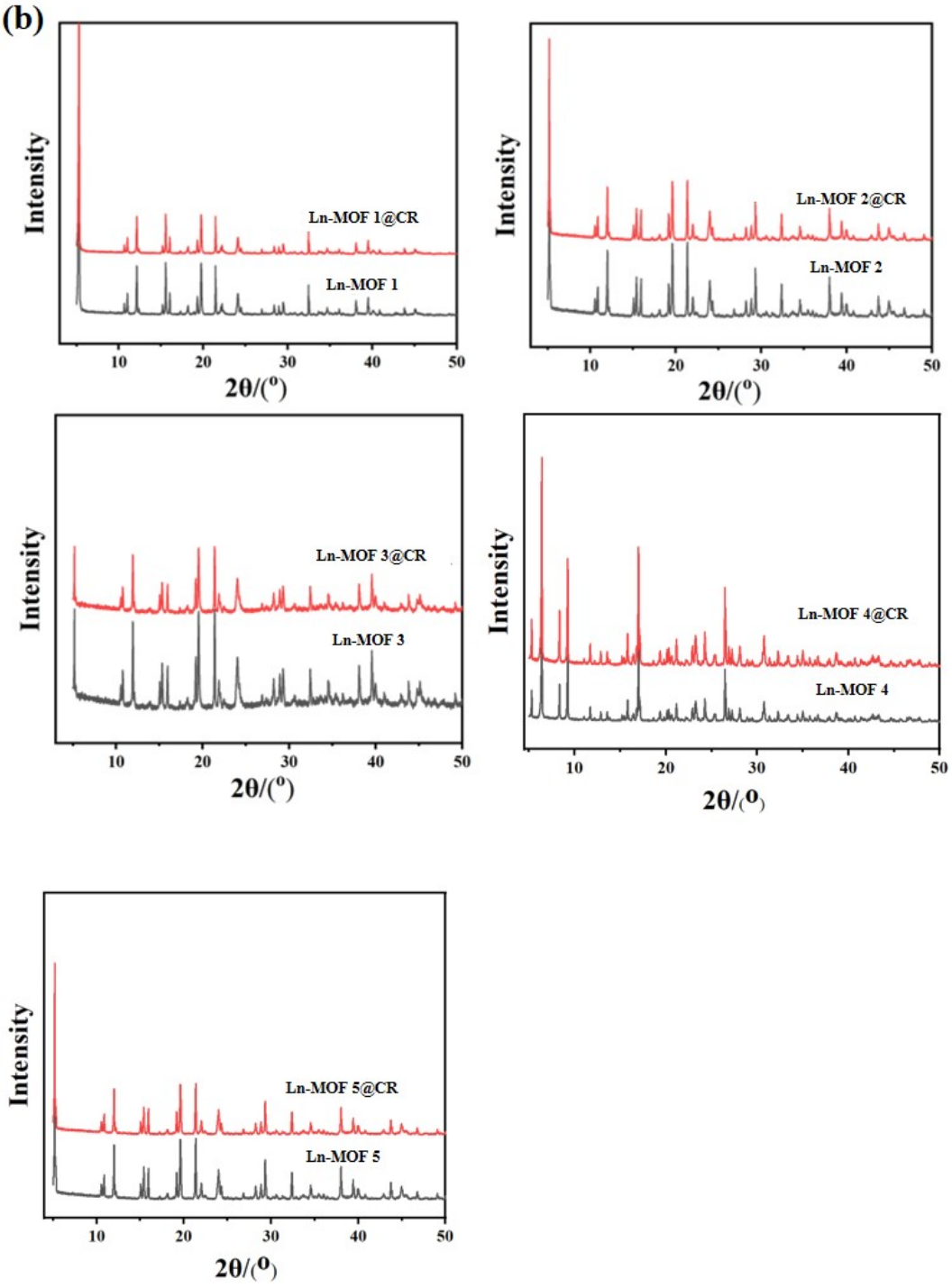


Fig. S1: (a) The experimental and simulated PXRD patterns of Ln-MOFs **1-5**. (b) PXRD of Ln-MOFs **1-5** before and after dye adsorption.

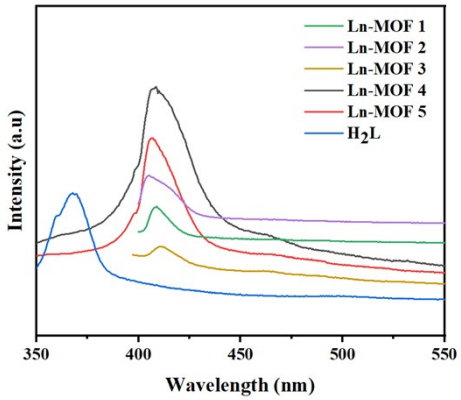
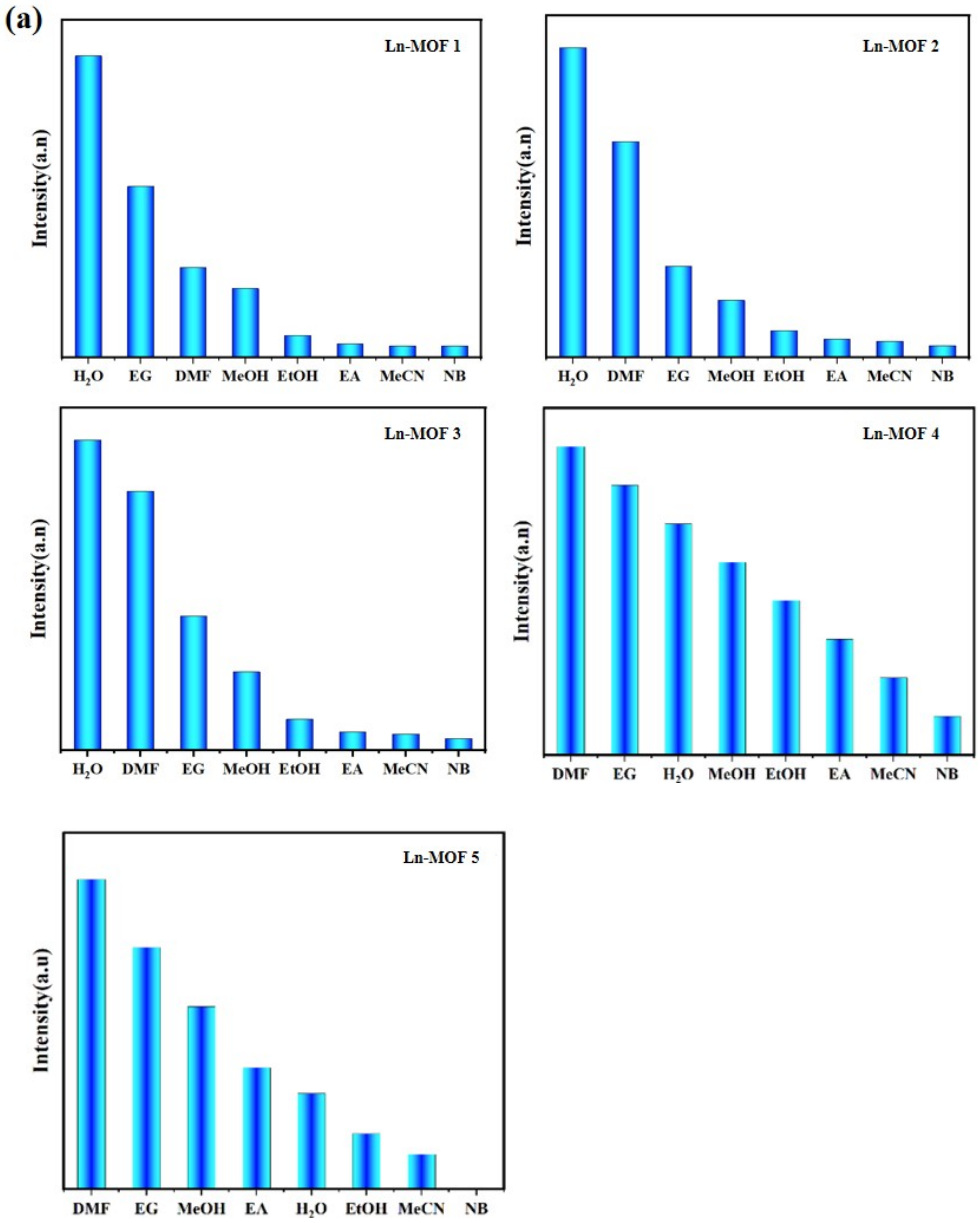


Fig. S2: Emission spectra of H_2**L** ligand and Ln-MOFs **1-5** at room temperature (λ_{ex} = 360 nm and 350 nm, respectively).



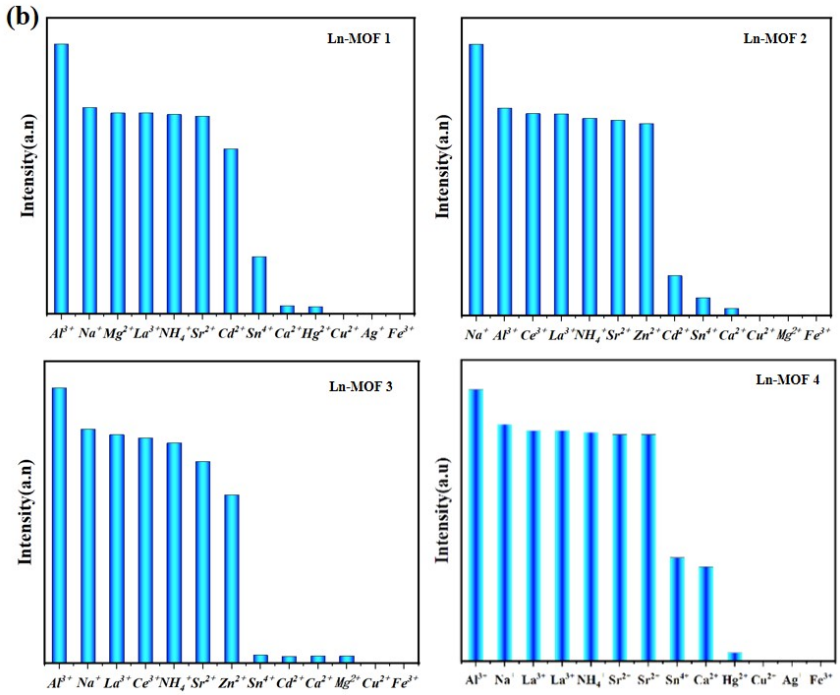
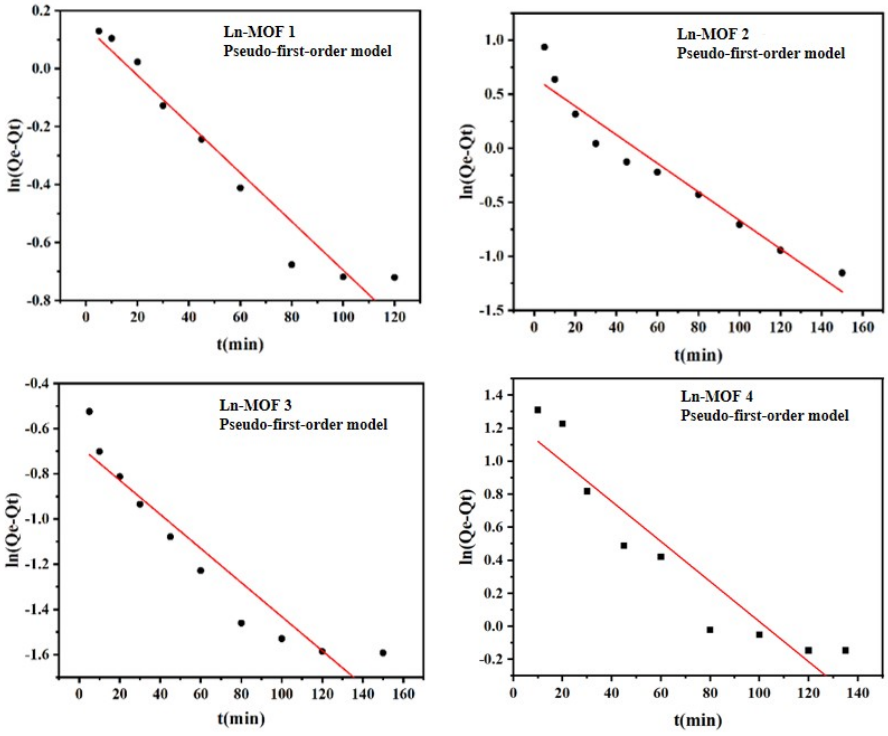


Fig. S3: (a) The fluorescence intensity of **1**-**5** in different solvents; (b) The fluorescence intensity of **1**-**4** in solutions containing various cations.



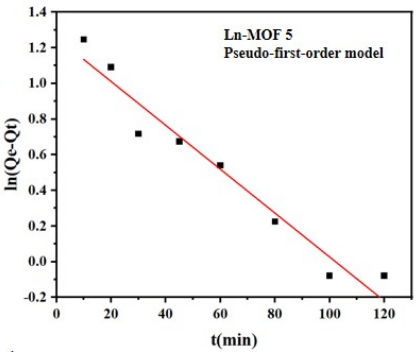


Fig. S4: Pseudo-first-order kinetic model for the adsorption of CR by Ln-MOFs **1**-**5**.

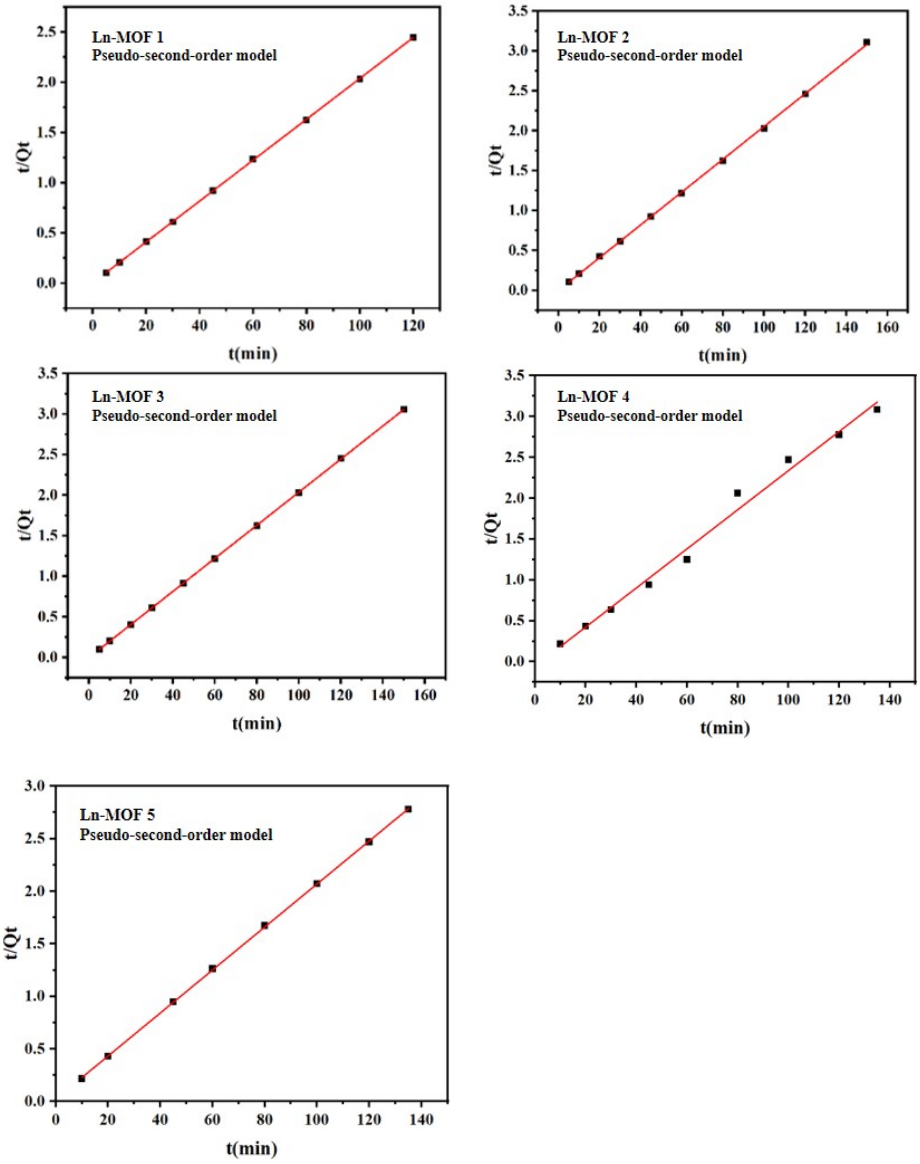


Fig. S5: Pseudo-second-order kinetic model for the adsorption of CR by Ln-MOFs **1**-**5**.

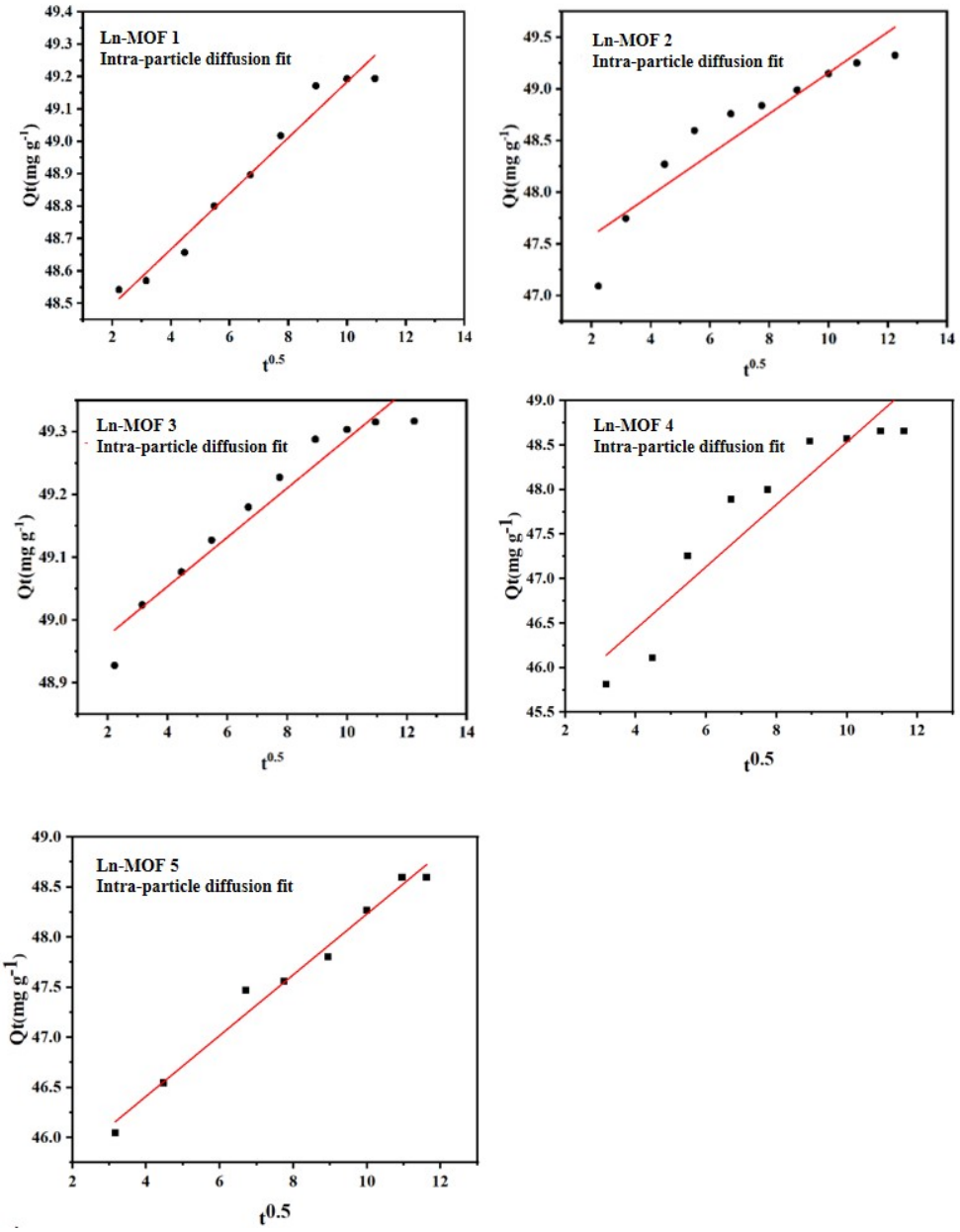
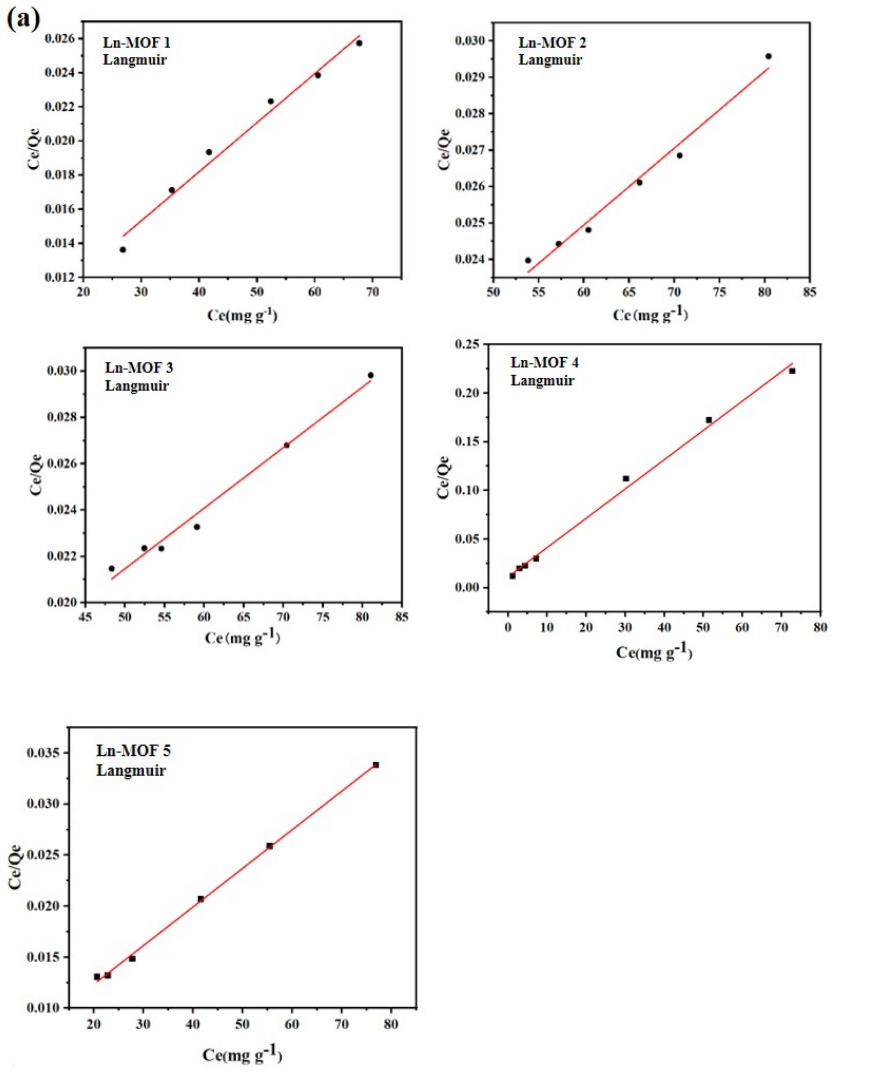
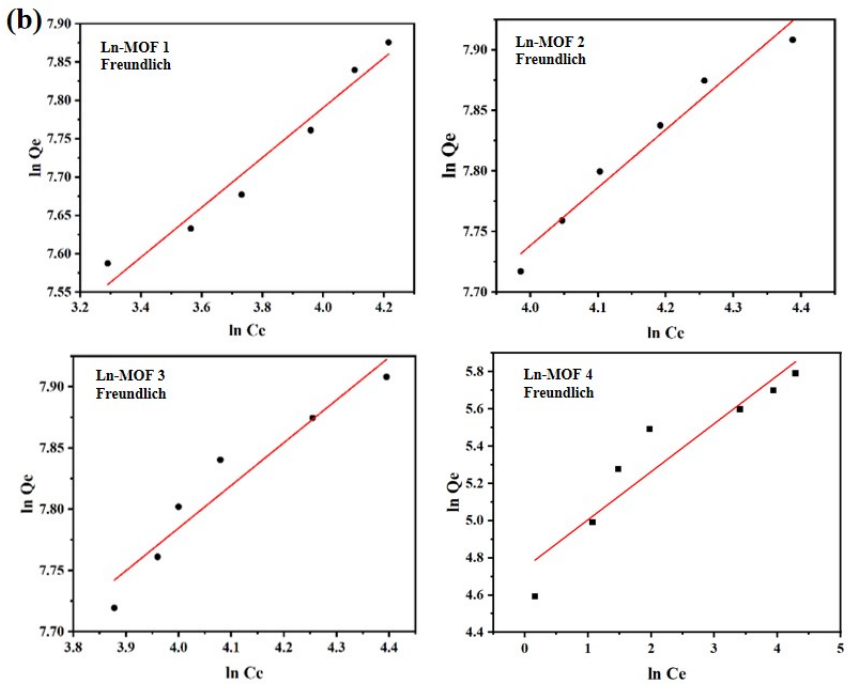


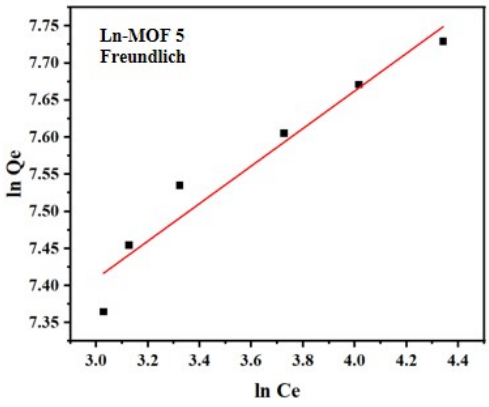
Fig. S6: Particle diffusion model for the adsorption of CR by Ln-MOFs **1**-**5**.

Table S3. Kinetic parameters of adsorption of CR by Ln-MOFs **1-5**

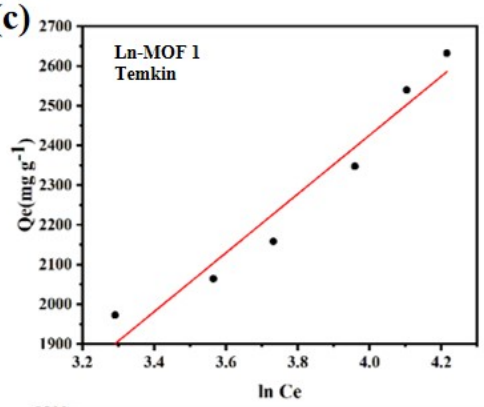
	The pseudo-first-order rate equation			The pseudo-second-order rate equation			Intra-particle diffusion equation		
	$\ln(Q_e-Q_t)=\ln Q_e-K_1t$			$t/Q_t=1/K_2Q_e^2+t/Q_e$			$Q_t=Kit^{0.5}+C$		
	$K_1(min^{-1})$	$Q_e(mg\ g^{-1})$	R^2	$K_2(min^{-1})$	$Q_e(mg\ g^{-1})$	R^2	K_i	C	R^2
1	0.0084	1.156	0.9409	0.0961	49.26	0.9999	0.086	48.32	0.9670
2	0.0132	1.923	0.9283	0.1547	48.66	0.9997	0.197	47.18	0.8517
3	0.0075	0.508	0.8848	0.179	49.02	0.9999	0.039	48.89	0.9314
4	0.0121	3.442	0.8703	0.011	41.81	0.9949	0.350	45.03	0.8649
5	0.0123	3.477	0.9439	0.017	48.89	0.9998	0.303	45.19	0.9798

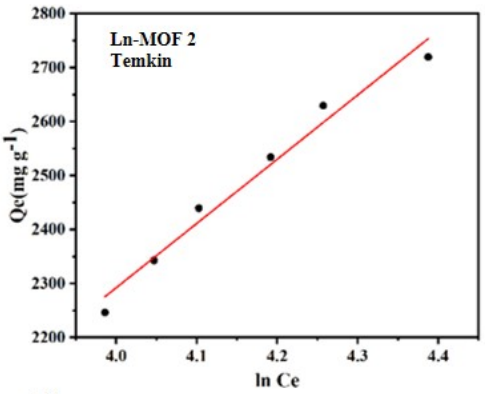

(a)
Ln-MOF 1
Langmuir
Ce/Qe
Ce(mg g-1)
Ln-MOF 2
Langmuir
Ce/Qe
Ce (mg g-1)
Ln-MOF 3
Langmuir
Ce/Qe
Ce (mg g-1)
Ln-MOF 4
Langmuir
Ce/Qe
Ce(mg g-1)
Ln-MOF 5
Langmuir
Ce/Qe
Ce(mg g-1)

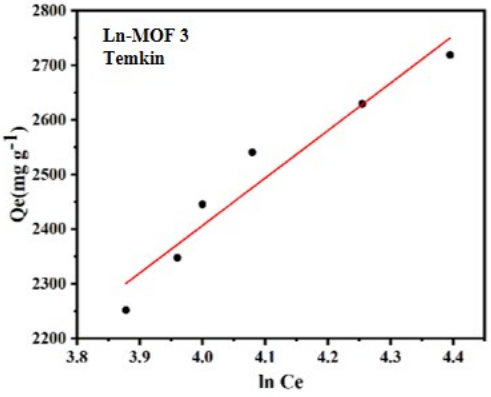

(b)
Ln-MOF 1
Freundlich
ln Qe
ln Ce
Ln-MOF 2
Freundlich
ln Qe
ln Ce
Ln-MOF 3
Freundlich
ln Qe
ln Ce
Ln-MOF 4
Freundlich
ln Qe
ln Ce

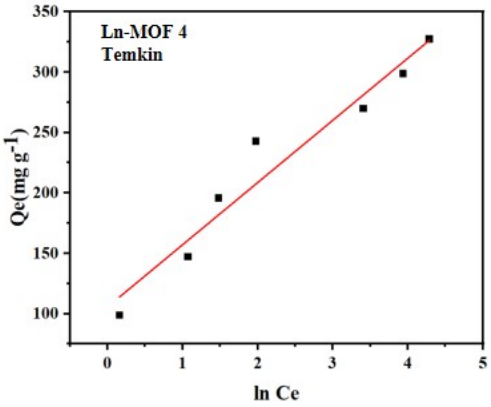

Ln-MOF 5
Freundlich
ln Qe
ln Ce

(c)


Ln-MOF 1
Temkin
Qe(mg g-1)
ln Ce


Ln-MOF 2
Temkin
Qe(mg g-1)
ln Ce


Ln-MOF 3
Temkin
Qe(mg g-1)
ln Ce


Ln-MOF 4
Temkin
Qe(mg g-1)
ln Ce

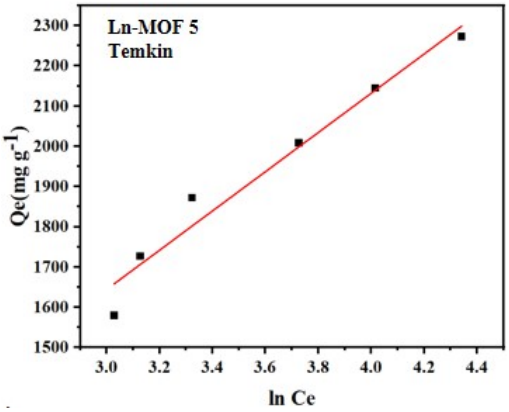

Ln-MOF 5
Temkin
Qe(mg g-1)
ln Ce

Fig. S7: (a) Fitting results of Langmuir model for CR adsorption by Ln-MOFs **1-5**; (b) Fitting results of Freundlich model for CR adsorption by Ln-MOFs **1-5**; (c) Fitting results of Temkin model for CR adsorption by Ln-MOFs **1-5**. $lnQ_e=BlnK_T+BlnC_e$

Table S4. Isotherm parameters of adsorption of CR by Ln-MOFs **1-5**

	Langmuir			Freundlich			Temkin		
	$C_e/Q_e=C_e/Q_m+1/Q_mK_L$			$lnQ_e=BlnK_T+BlnC_e$			$Q_e=lnK_F+b_FlnC_e$		
	K_L(L mg^{-1})	Q_m(mg g^{-1})	R^2	K_F(mg g^{-1})	b_F	R^2	K_T	B	R^2
1	0.00029	3448	0.9832	657	0.32	0.9545	0.4857	740	0.9381
2	0.00028	3571	0.9814	336	0.47	0.9597	0.1255	1190	0.9698
3	0.00027	3703	0.9858	595	0.35	0.9053	0.2922	869	0.9209
4	0.00301	332	0.9939	115	0.25	0.8643	7.7194	51	0.9391
5	0.00038	2645	0.9984	757	0.25	0.9285	1.4514	487	0.9543