Supporting Information

Metal-organic Frameworks of MIL-100(Fe, Cr) and MIL-101(Cr) for Aromatic Amines Adsorption from Aqueous Solutions

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Supporting Information

Synthesis and activation of MIL-100(Cr)

3.6 g $Cr(NO_3)_3 \cdot 9H_2O$, 1.35 g 1,3,5-benzenetricarboxylic acid, 60 mL of H_2O were added to teflon-lined steel autoclaves and maintained at 220℃ for 96 h. After cooling, the sample was washed with water and activated by thermal treatment at 150 ℃ [S1].

Synthesis and activation of MIL-101(Cr)

Terephthalic acid (1.64 g)，$Cr(NO_3)_3 \cdot 9H_2O$ (4 g) and H_2O (60 mL) were added to teflon-lined steel autoclaves and maintained at 220 ℃ for 8 h [S2]. After cooling，the as-synthesized MIL-101 was further purified by hot ethanol, H_2O and acetone solutions. After drying at 80 °C，MIL-101 was vacuum dried at 150 °C overnight.

[S1] Gérard, F.; Christian, S.; Caroline, M.D.; Franck, M.; Suzy, S.; Julien, D.; Irène, M. A hybrid solid with giant pores prepared by a combination of targeted chemistry, simulation, and powder diffraction[J]. Angewandte Chemie Int Ed, 2010, 116: 6456-6461.

[S2] Hwang, Y.K.; Hong, D.Y.; Chang, J.S.; Jhung, S.H.; Seo, Y.K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Férey, G. Titelbild: Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation [J]. Angewandte Chemie Int Ed, 2010, 47: 4144-4148.

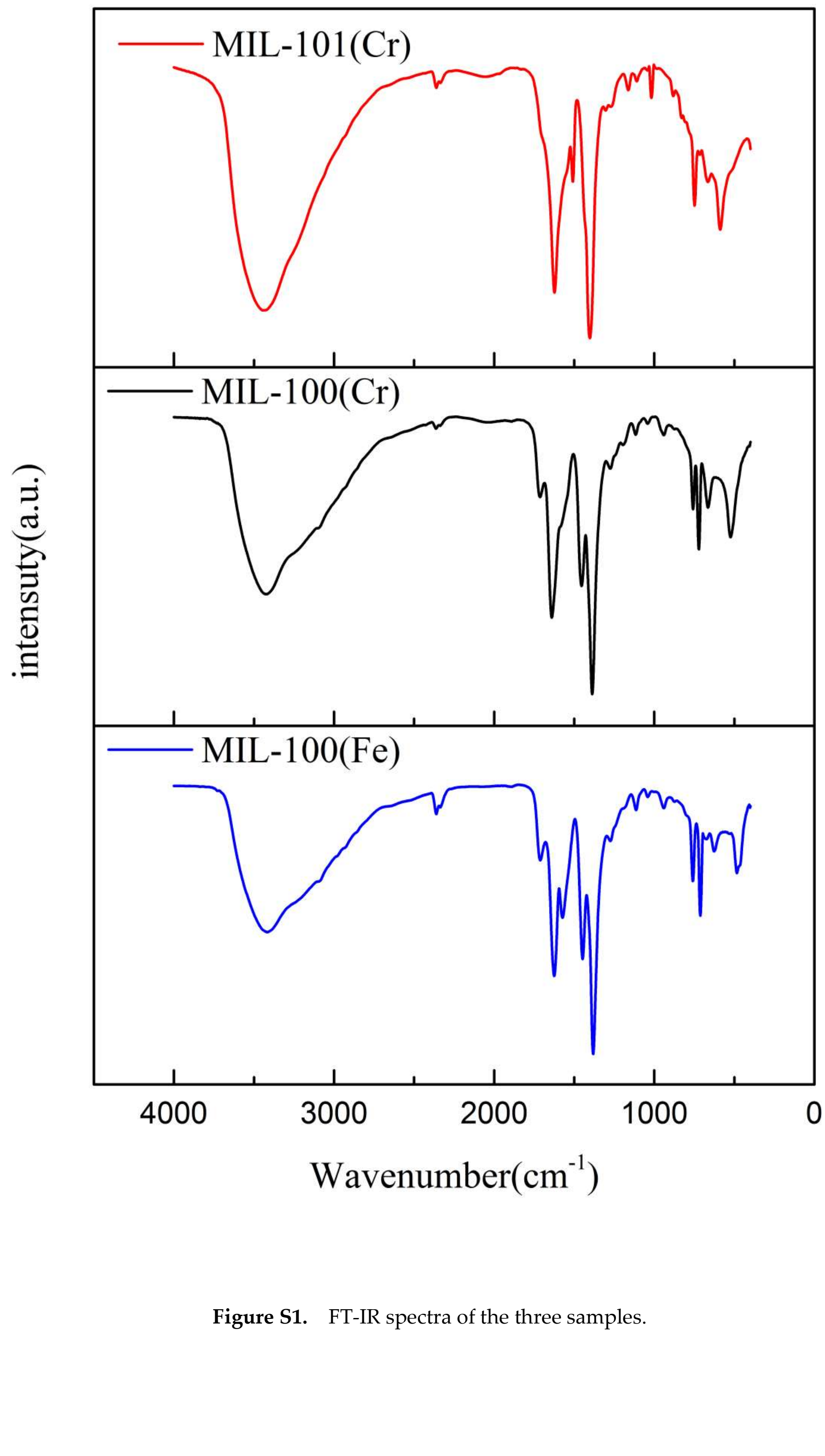
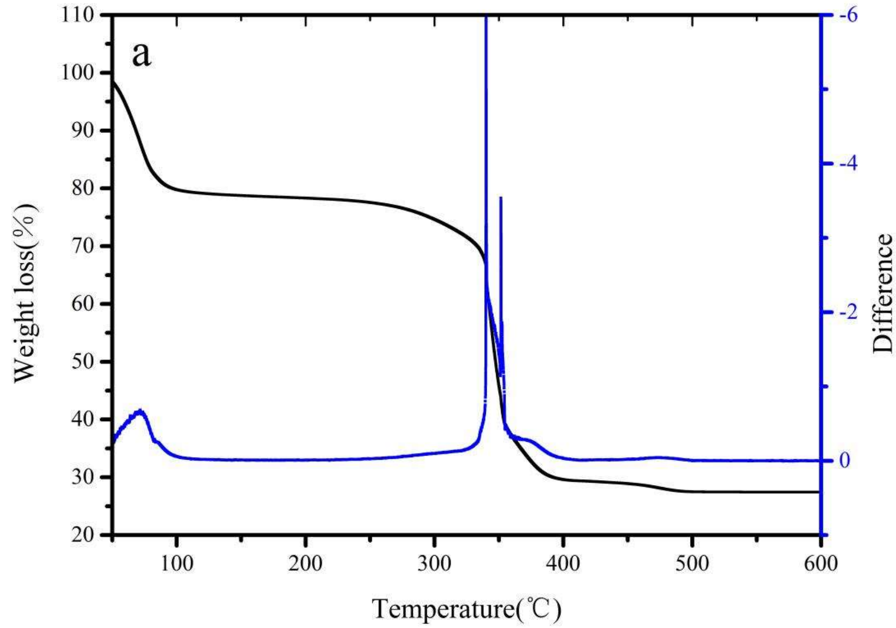
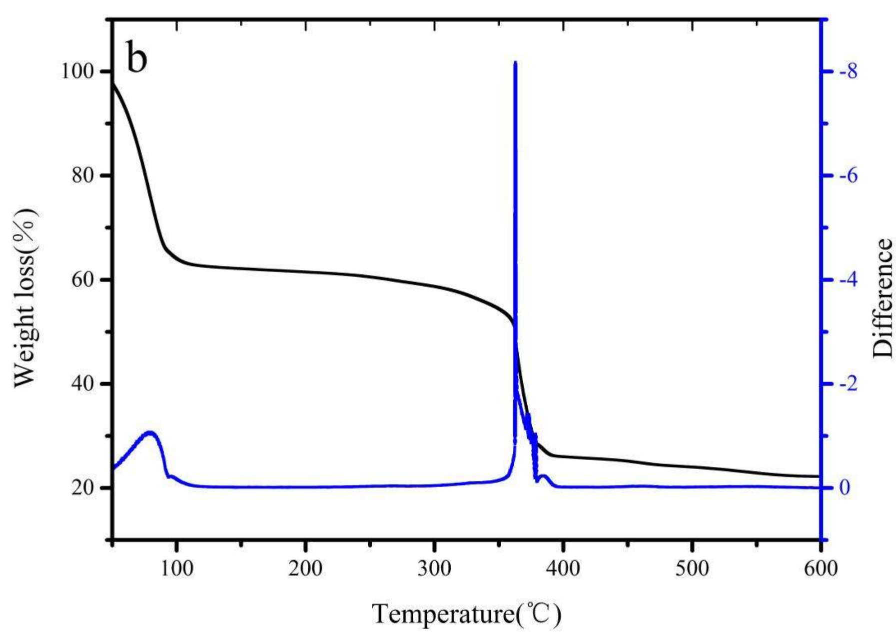


Figure S1. FT-IR spectra of the three samples.


a
Weight loss(%)
110
100
90
80
70
60
50
40
30
20
Difference
-6
-4
-2
0
100
200
300
400
500
600
Temperature(℃)


b
Weight loss(%)
100
80
60
40
20
Difference
-8
-6
-4
-2
0
100
200
300
400
500
600
Temperature(℃)

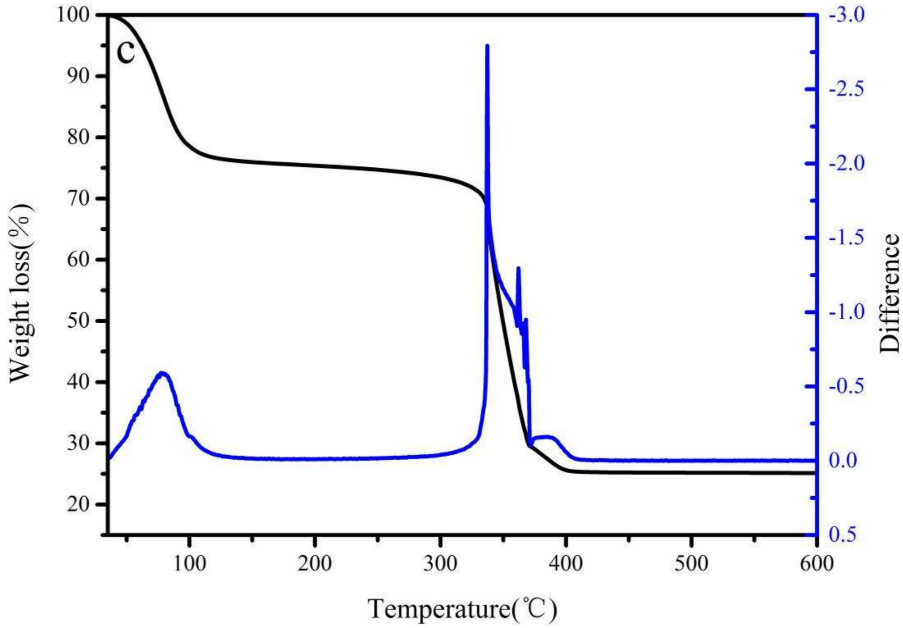


Figure S2. TG-DTG curves of (a)MIL-100(Cr) (b) MIL-101(Cr) and (c)MIL-100(Fe)

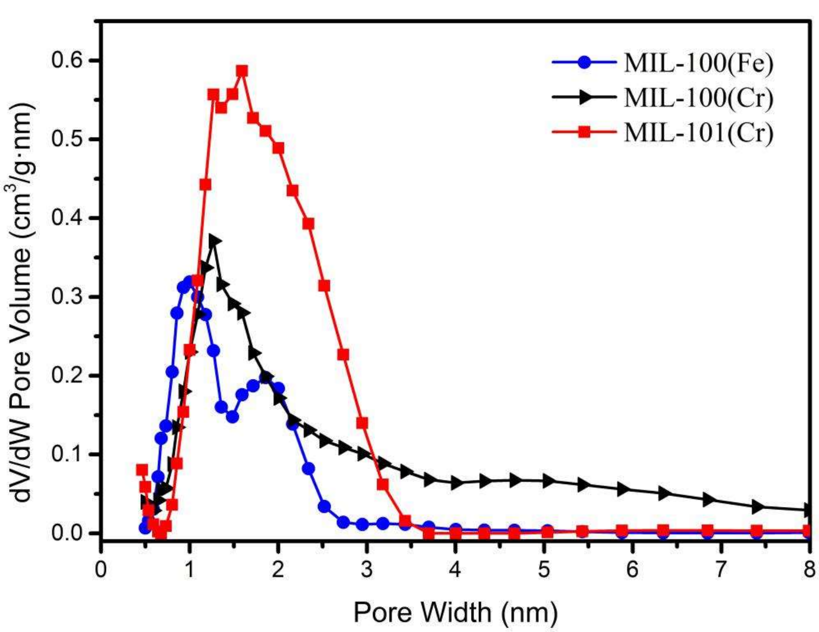
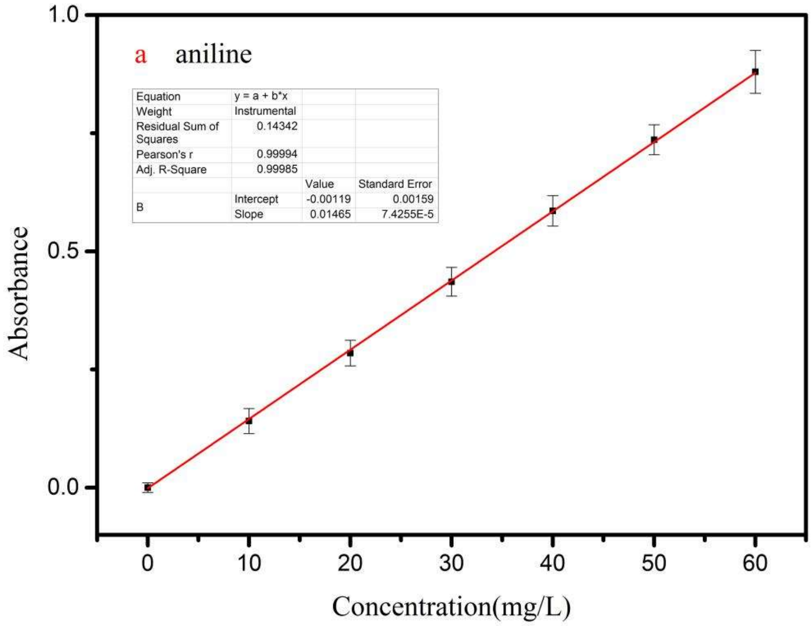
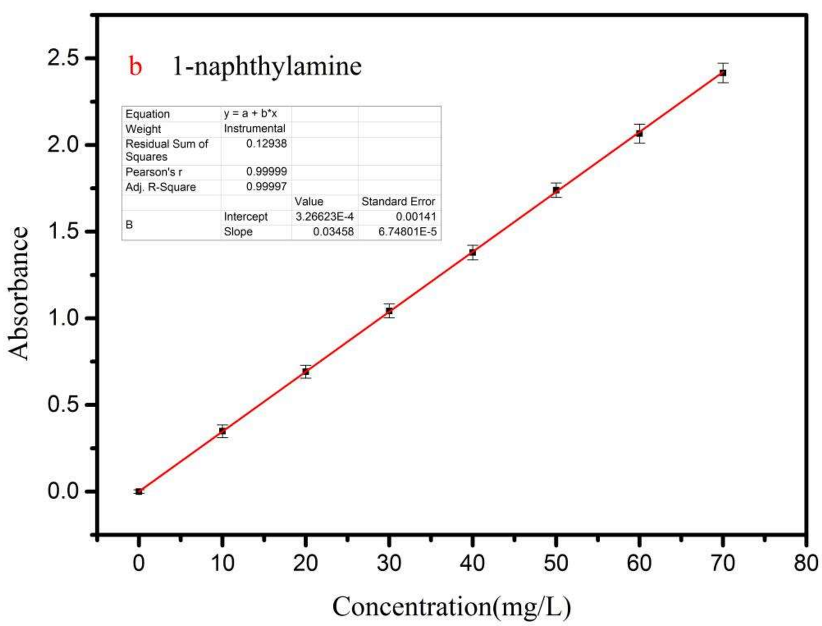


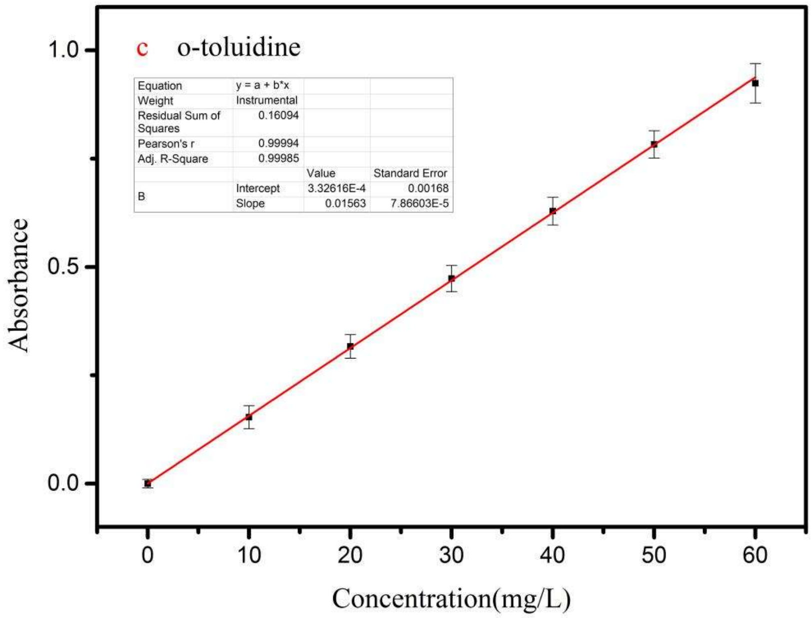
Figure S3. The pore size distribution of MIL-100(Fe) (blue), MIL-100(Cr)(black) and MIL-101(Cr) (red).

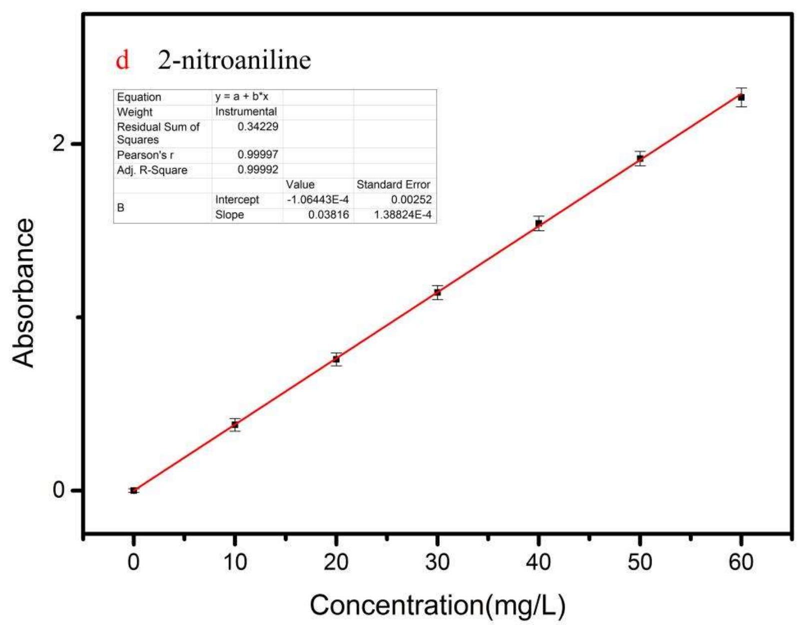


a aniline
Equation | y = a + b*x
Weight | Instrumental
Residual Sum of Squares | 0.14342
Pearson's r | 0.99994
Adj. R-Square | 0.99985
Value | Standard Error
B | Intercept | -0.00119 | 0.00159
B | Slope | 0.01465 | 7.4255E-5
Absorbance
Concentration(mg/L)



b 1-naphthylamine
Equation | y = a + b*x
Weight | Instrumental
Residual Sum of Squares | 0.12938
Pearson's r | 0.99999
Adj. R-Square | 0.99997
Value | Standard Error
B | Intercept | 3.26623E-4 | 0.00141
B | Slope | 0.03458 | 6.74801E-5
Absorbance
Concentration(mg/L)


c o-toluidine
Equation y = a + b*x
Weight Instrumental
Residual Sum of Squares 0.16094
Pearson's r 0.99994
Adj. R-Square 0.99985
Value Standard Error
B Intercept 3.32616E-4 0.00168
Slope 0.01563 7.86603E-5
Absorbance
Concentration(mg/L)
1.0
0.5
0.0
0
10
20
30
40
50
60


d 2-nitroaniline
Equation y = a + b*x
Weight Instrumental
Residual Sum of Squares 0.34229
Pearson's r 0.99997
Adj. R-Square 0.99992
Value Standard Error
B Intercept -1.06443E-4 0.00252
Slope 0.03816 1.38824E-4
Absorbance
Concentration(mg/L)
2
0
0
10
20
30
40
50
60

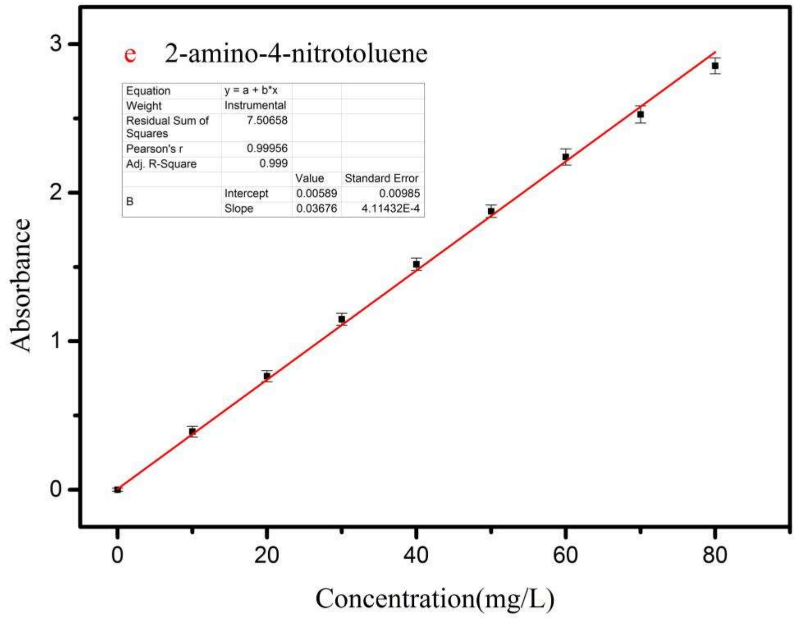


Figure S4. The calibration curves of (a)aniline (b)1-naphthylamine (c)o-toluidine (d)2-nitroaniline (e)2-amino-4-nitrotoluene

Aqueous stock solutions of Aromatic amine (100mg/L) were prepared by dissolving Aromatic amine in Milli-Q water. Aqueous solutions with different concentrations(10-80mg/L) of Aromatic amine were prepared by serial dilution of the stock solution with Milli-Q water. The Absorbance of aromatic amine solution were determined using UV-vis spectrophotometer (Shimadzu UV-2550) at 280 nm. Standard curve is established by known concentrations of aromatic amines and absorbance.

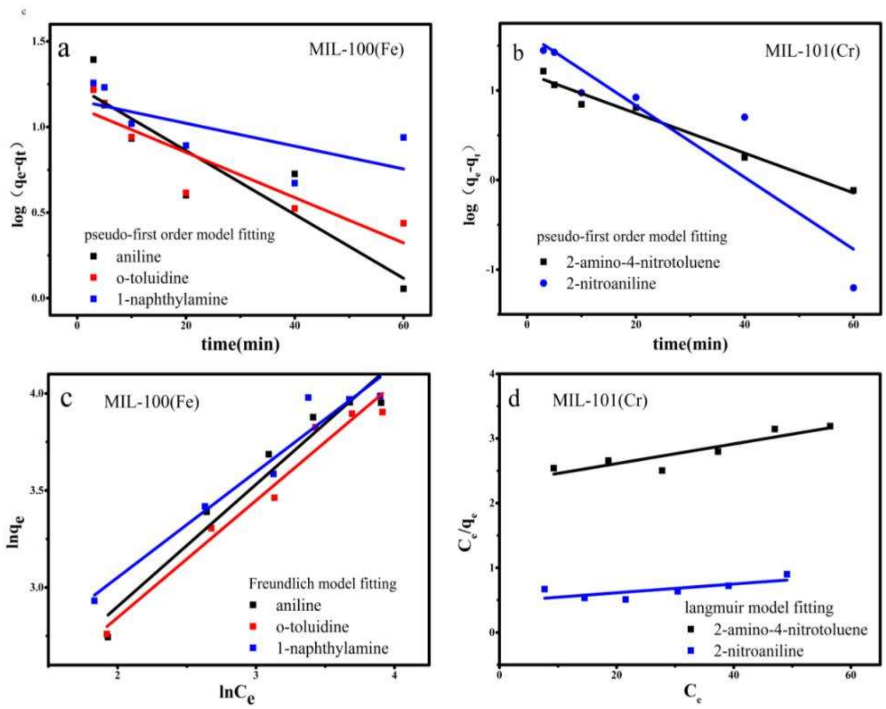


Figure S5. (a)(b) The pseudo first-order kinetic model of MIL-100(Fe) and MIL-101(Cr).(c) Isothermal Freundlich model of MIL-100(Fe)(d)Isothermal Langmuir model of MIL-101(Cr).

Table.S1. Thermal analysis data of MIL-100(Fe,Cr), MIL-101(Cr).

Entry	Loss1,water molecules	Loss 2, organic ligands	Calculated residues
MIL-100(Cr)	76 °C, 79.3%	341 °C, 27.6%	Cr_2O_3, 27.5%
MIL-101(Cr)	81 °C, 62.5%	362 °C, 22.6%	Cr_2O_3, 20.9%
MIL-100(Fe)	84 °C, 75%;	345 °C, 25.2%	Fe_2O_3, 28.5%

Table S2. surface area, pore volume, pore size of the,MIL-100(Fe,Cr),MIL-101(Cr).

Samples	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore width (nm)
MIL-100(Fe)	1018	0.67	1.14
MIL-100(Cr)	1427	1.39	1.26
MIL-101(Cr)	2134	1.15	1.61

Table.S3.the measurements for each combination of MOF and aniline derivative.(mg/g)

MOFs	Initial concentration(mg/L)	Capacity of aromatic amines by MOFs(mg/g)														
		aniline			1-naphthylamine			o-toluidine			2-nitroaniline			2-amino-4-nitrotoluene		
MIL-100(Fe)	10	13.68	15.55	17.14	18.75	19.24	17.63	15.80	14.46	17.11	0	0.21	0	1.45	2.14	0.62
	20	27.25	29.65	31.87	30.50	31.97	28.89	27.25	28.30	30.45	0.50	0.21	0.46	1.62	0.78	2.68
	30	37.27	39.90	41.07	36.05	37.26	35.08	35.25	34.15	38.35	0.50	0.43	0.14	1.76	2.77	0.98
	40	46.43	48.30	50.98	53.45	53.97	49.01	45.85	45.90	37.15	3.80	3.12	3.91	1.91	2.39	0.41
	50	49.52	52.15	54.59	52.95	56.93	48.96	49.20	50.05	42.60	3.00	3.33	2.85	2.48	1.29	2.51
	60	46.06	52.05	53.97	53.90	56.75	48.71	49.60	47.40	54.45	3.70	3.31	3.60	2.67	3.37	2.08
	70				53.20	55.94	50.07							3.02	3.54	2.44
	80													2.87	3.36	2.02
MIL-100(Cr)	10	8.80	10.54	5.58	12.75	14.55	12.20	0	0.14	0	0.52	0	0.58	3.65	2.52	4.47
	20	13.40	14.86	9.95	20.35	19.50	16.65	2.00	2.55	1.45	1.00	1.34	0.83	4.40	5.51	3.34
	30	15.40	12.17	15.83	27.25	29.30	24.50	7.80	5.55	10.15	3.35	4.21	3.22	5.35	6.53	4.19
	40	20.05	22.40	16.79	25.85	29.87	22.18	10.20	6.50	13.5	1.45	1.96	1.38	7.65	6.24	8.86
	50	22.75	25.70	18.05	25.00	32.18	20.02	13.75	8.71	17.46	7.45	5.23	7.88	7.00	5.37	8.77
	60	23.80	27.93	18.76	24.50	30.36	21.08	13.05	14.5	8.15	9.30	9.68	7.61	7.30	7.79	5.37
	70				25.50	31.20	22.28							9.75	8.56	11.08
	80													7.30	7.28	9.61
MIL-101(Cr)	10	6.70	7.61	5.76	12.95	13.98	11.45	5.95	4.73	7.97	11.50	11.30	12.10	3.65	4.27	2.73
	20	14.00	15.24	10.75	25.75	26.94	24.40	21.45	21.90	14.15	27.30	28.20	26.25	7.00	6.74	7.63
	30	14.15	10.07	17.91	34.50	31.50	34.50	36.4	35.15	39.30	42.25	41.80	44.85	11.1	10.31	11.75
	40	16.95	20.82	12.68	37.20	34.85	36.50	44.05	39.65	48.91	47.85	46.80	51.20	13.35	15.66	12.35
	50	19.65	21.77	17.19	37.20	42.75	33.26	44.10	42.45	49.80	54.30	54.20	59.60	14.95	13.97	15.96
	60	19.30	21.88	17.37	37.35	39.74	30.90	43.60	41.10	49.30	54.55	53.15	60.25	17.7	19.23	16.37

70	38.85	43.9	35.65	25.55	26.65	23.97
80				25.1	26.78	23.84