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Ni(II) and Co(II) complexes for the selective adsorption of anionic dyes from aqueous solutions

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Supplementary Index

1. Materials and methods

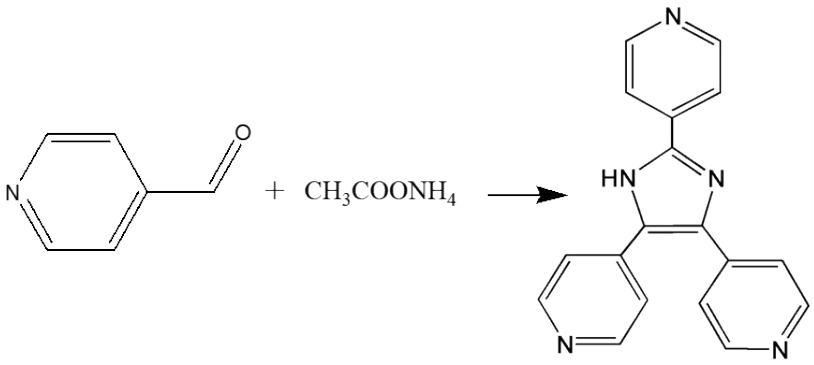
All other chemicals purchased were of reagent grade or better and used without further purification. The elemental analyses for C, H and N were carried out on a Perkin Elmer 240C automatic analyzer. The 1H-NMR spectra were measured on Nuclear Magnetic Resonance Spectrometer (Bruker Avance II 400). Infrared spectra were measured on a Bruker AXS TENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 4000-400 cm^{-1}. UV-vis absorption spectra were recorded with a JASCO V570 UV/VIS/NIR spectrophotometer (200-800 nm, in the form of solid sample) and with UV-1000 spectrometer (200-800 nm, in the form of liquid sample). X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Advance-D8 equipped with Cu-Kα radiation, in the range of $5° < 2\theta < 60°$, with a step size of 0.02° (2θ) and a count time of 2s per step. Thermogravimetric analyses (TG) were performed under nitrogen atmosphere with a heating rate of 10°C/min on a Perkin Elmer Diamond TG/DTA. Also, Jade 5 software was used to calculate the area ratio of crystallization and non-crystallization by removing the background to calculate the crystallinity of the complexes **1** and **2**. The zeta potential of the complexes **1** and **2** before and after dye adsorption was investigated by the Malvern 3000 equipment (England).

2. X-ray Crystallographic Determination

Suitable single crystals of the two complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å)[1]. All the measure independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied by SADABS platform[2]. Crystal structures were solved by the direct method using OLEX 2 and SHELXL-97. PLATON eliminated the diffraction contribution of disordered guest molecules of complex **1** and analyzed the residual electron density. The results show that there are 45 electrons in each structural unit of complex **1**. Two H_2O molecules were added directly to the final molecular formula according to the SQUEEZE calculation as well as elemental analysis and thermogravimetric analysis. The details of the crystal parameters, data collection, and refinement for the complexes **1** and **2** are summarized in Table S4, and selected bond lengths are listed in Table S5.

3. The synthesis of 5-tri (4-pyridyl) -imidazole

The synthesis method of the Htpim ligand was referred to in the literature[3]. 2.14g (20 mmol) pyridine-4-formaldehyde and 3.08 g (40 mmol) CH_3COONH_4 were placed in a high-pressure reaction kettle and reacted in an oven at 120 ℃ for three days. After the reaction, the yellow product was washed with 50 mL distilled water and recrystallized with appropriate amount of ethanol after drying. After filtration and drying, 1.20 g yellow solid was obtained (Scheme 1). Yield: 65%. Molecular Formula: $C_{18}H_{13}N_5$ (299.0), Elemental analysis (%): Calcd. for (%) C, 72.21; H, 4.35; N, 23.41; Found (%) C, 72.22; H, 4.34; N, 23.40. ^{1}H-NMR (400 MHZ, DMSO-d6): δ 13.48 (s, 1H), 8.72 (d, J = 6.0 Hz, 4H), 8.53 (dd, J = 18.8, 4.9 Hz, 2H), 8.05 (t, J = 11.6 Hz, 2H), 7.54 (s, 4H) (Figure S1). IR data (KBr, cm^{-1}): 3125, 3040, 1663, 1602, 1428, 1140, 1069, 735 (Figure S3a).



Scheme 1 Synthesis of the Htpim ligand.

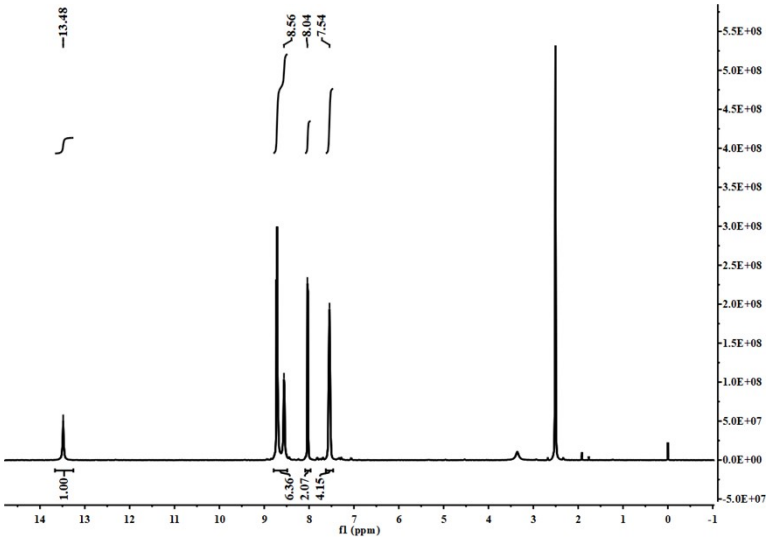


Figure S1 The ^{1}H-NMR spectrum of Htpim ligand.

4. IR spectra

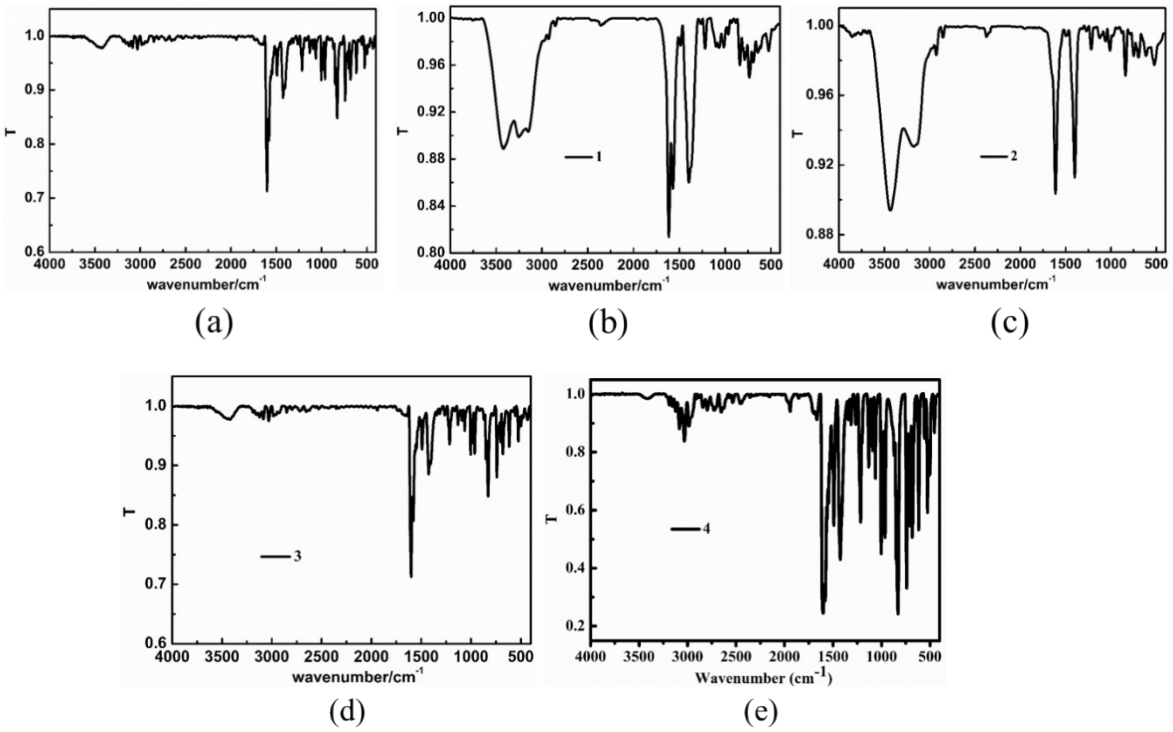


Figure S3 IR spectra: (a) Ligand Htpim; (b) Complex **1**; (c) Complex **2**; (d) Compound **3**; (d) Compound **4**;

Table S1 IR spectra (cm^{-1}) of ligand Htpim, complexes **1-2** and compounds **3-4.**

Compounds	Htpim	**1**	**2**	**3**	**4**
ν_{OH}		3426	3437	3424	3409
ν_{NH}	3125	3256	3183	3130	3123
ν_{Ar-H}	3040	3136	2929	3092	3038
$\nu_{C=N}$	1663	1620	1610	1673	1673
$\nu_{C=C}$	1602, 1428	1564, 1404	1584, 1492	1600, 1418	1604, 1426
ν_{C-C}	1140	1229	1130	1140	1133
ν_{C-N}	1069	1085	1064	1055	1058
δ_{Ar-H}	735	744	761	732	747

5. UV-Vis spectra

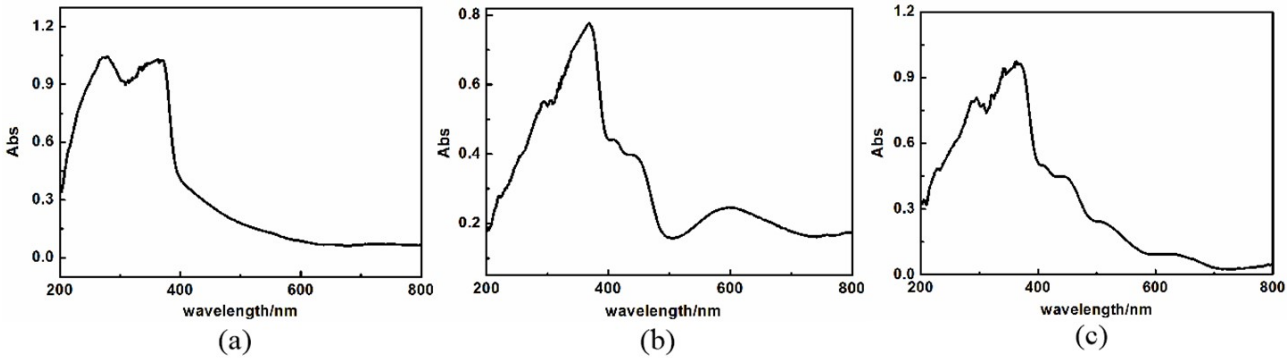


Figure S4 UV-Vis spectra: (a) Ligand Htpim; (b) Complex **1**; (c) Complex **2**.

Table S2 UV-Vis spectra data (nm) of ligand Htpim and complexes **1** and **2**

	Htpim	**1**	**2**
π-π*	272	292	292
n-π*	366	369	368
LMCT		409	408
MMCT		441 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	447 $^4T1_g(F) \rightarrow {}^4A_{2g}(F)$
		596 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	512 $^4T1_g(F) \rightarrow {}^4T_{1g}(F)$
		789 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	628 $^4T1_g(F) \rightarrow {}^4T_{2g}(F)$

6. TG spectra

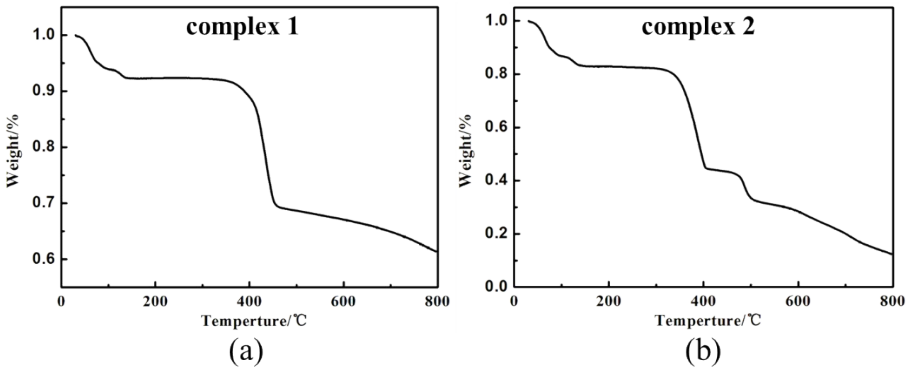


Figure S5 TG curves: (a) Complex **1**; (b) Complex **2**

Table S3 TG analysis of complexes **1** and **2**

Complex		First weightlessness stage	Second weightlessness stage	Third weightlessness stage	Residuum
1	Temperature (°C)	30-180	340-455	-	NiO and C
	Weightlessness identify	two H_2O molecules, one HCl	part of Htpim collapsed		
	Actual weight loss rate (%)	9.0	75.5		
	Theoretical weight loss rate (%)	9.3	-		
2	Temperature (°C)	30-135	300-400	400-500	CoO and C
	Weightlessness identify	two H_2O molecules	one HCl, Htpim	part of Htpim collapsed	
	Actual weight loss rate (%)	16.2	38.0	10.1	
	Theoretical weight loss rate (%)	15.2	37.8	-	

7. PXRD patterns

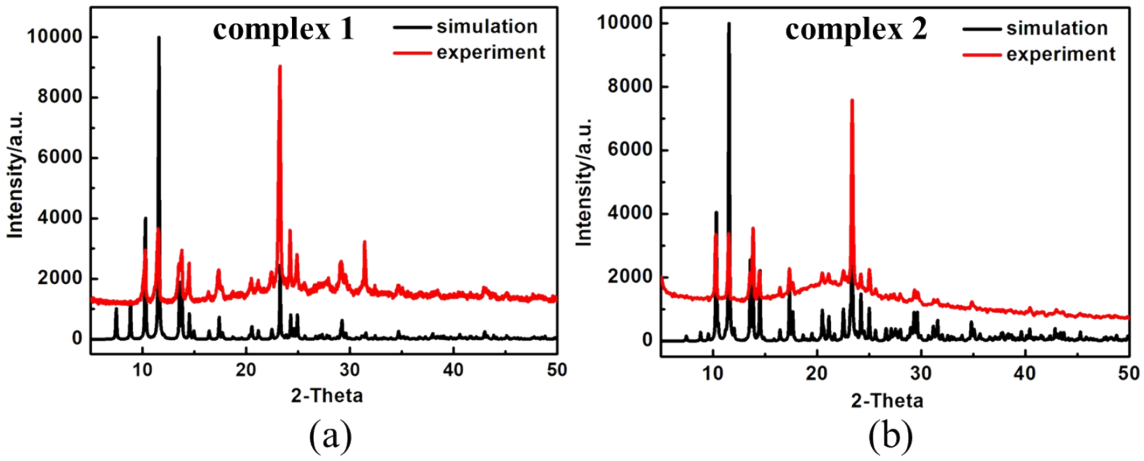


Figure S6 PXRD patterns: (a) Complex **1**; (b) Complex **2**

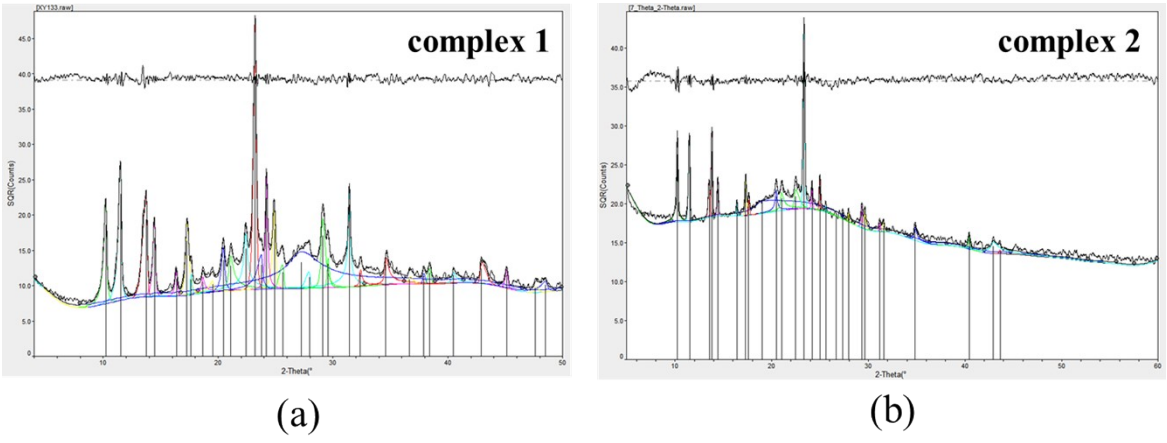


Figure S7 The crystallinity rate: (a) Complex **1**; (b) Complex **2**.

8. Adsorption Experiments

Table S4 Correlation data of kinetics fitted to adsorption of CBB dyes by complexes **1** and **2**.

Complexes	Dose (mg)	Pseudo fist-order kinetics model		Pseudo secondary-order kinetics model	
		k_1 (min^{-1})	R^2	k_2 (g/(mg·min))	R^2
1	2.5	1.289×10^{-2}	**0.9887**	3.978×10^{-4}	**0.9968**
	5	1.059×10^{-1}	**0.7514**	7.797×10^{-3}	**0.9996**
	10	5.043×10^{-2}	**0.8008**	6.430×10^{-4}	**0.9946**
2	10	1.865×10^{-2}	**0.9130**	1.829×10^{-3}	**0.9928**
	15	6.218×10^{-2}	**0.4960**	1.000×10^{-2}	**0.9989**
	20	1.151×10^{-2}	**0.9067**	2.027×10^{-3}	**0.9967**
	15	1.312×10^{-2}	**0.6995**	4.727×10^{-3}	**0.9997**

Table S5 Correlation data of kinetics fitted to adsorption of Eosin dyes by the complexes **1** and **2**.

Complexes	Dose (mg)	Pseudo secondary-order kinetics model		Pseudo secondary-order kinetics model	
		k_1 (min^{-1})	R^2	k_2 (g/(mg·min))	R^2
1	2.5	1.473×10^{-2}	**0.4167**	4.719×10^{-2}	**0.9997**
	5	1.197×10^{-2}	**0.5709**	2.256×10^{-2}	**0.9958**
	10	1.750×10^{-2}	**0.7691**	2.770×10^{-3}	**0.9962**
2	10	1.105×10^{-2}	**0.8184**	4.659×10^{-3}	**0.9901**
	15	3.224×10^{-3}	**0.9103**	3.182×10^{-3}	**0.9955**
	20	1.890×10^{-1}	**0.9099**	4.561×10^{-3}	**0.9983**

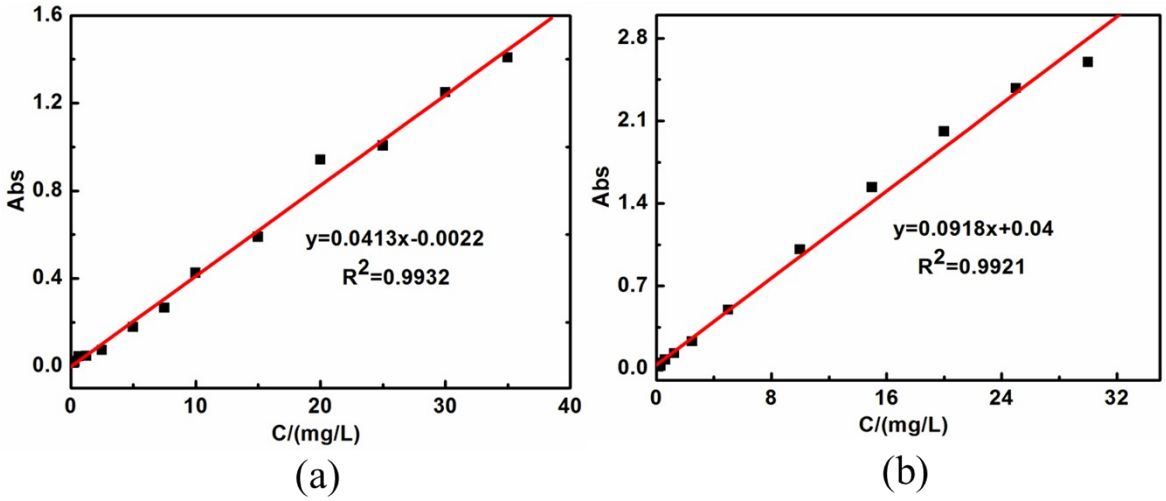


Figure S8 Standard curve of dyes: (a) CBB; (b) Eosin

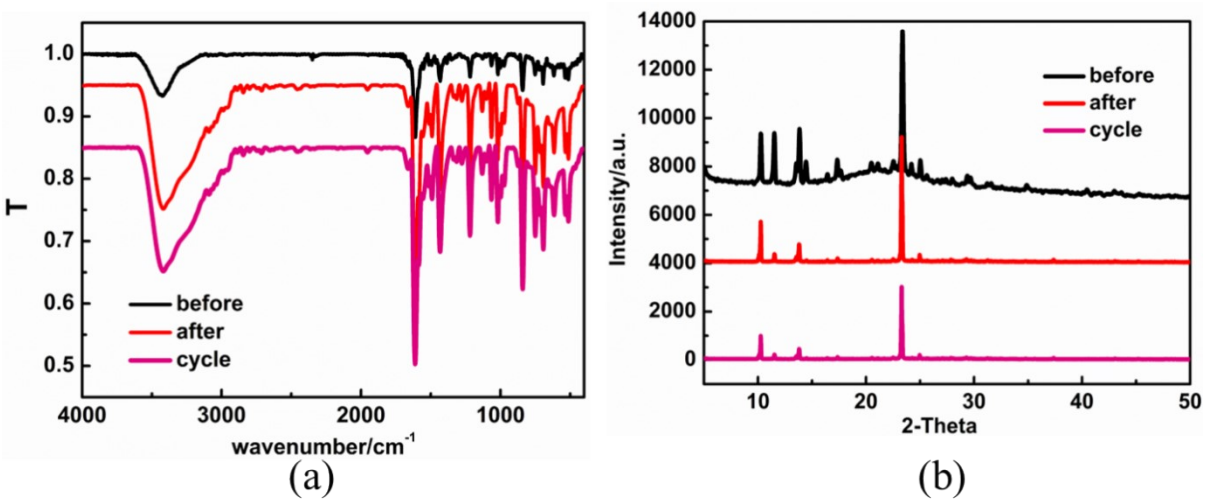


Figure S9 The IR spectra and PXRD spectra before and after adsorption, and cycle experiment.

9. SEM

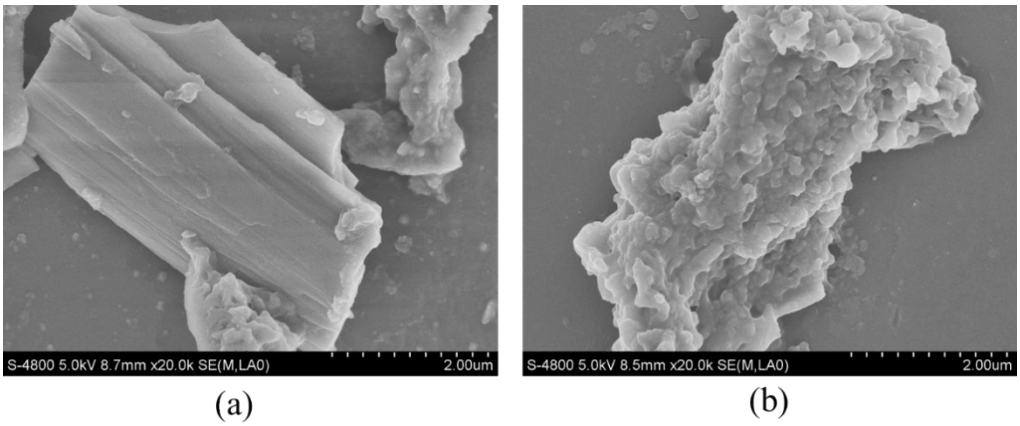


Figure S10 The image of SEM: (a) Before absorption; (b) After absorption.

10. Crystal data

Table S5 Major bond lengths for complexes **1** and **2** (Å)*.

Complex **1**			
Ni(1)-Cl(1)	2.3370 (16)	Ni(1)-N(1)$^{\#3}$	2.122 (3)
Ni(1)-Cl(1)$^{\#1}$	2.3370 (16)	Ni(1)-N(3)$^{\#1}$	2.113 (3)
Ni(1)-N(1)$^{\#2}$	2.1220 (3)	Ni(1)-N(3)	2.113 (3)
Complex **2**			
Co(1)-Cl(1)	2.4255 (13)	Co(1)-N(3)$^{\#1}$	2.172 (3)
Co(1)-N(1)	2.174 (3)	Co(1)-N(4)$^{\#2}$	2.167 (3)
Co(1)-N(2)	2.166 (3)	Co(1)-O(1)	2.250 (3)

*Symmetry codes: complex **1**: #1, 1-x, y, -1/2-z; #2, 1-x, -1+y, -1/2-z; #3, x, -1+y, z; complex **2**: #1, x, -1+y, z; #2, x, 1+y, z.

References

[1] SMART and SAINT (software packages); Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

[2] Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction for Area Detector Data, University of Gottingen, Gottingen, Germany, 1996.

[3] Li, Wang, Wen, et al. Syntheses, Structures, and Photoluminescent and Magnetic Properties of Four Novel Complexes Constructed from 2,4,5-Tri(4-pyridyl)-imidazole and Benzene-1,3,5-tricarboxylic Acid[J]. Zeitschrift Für Anorganische Und Allgemeine Chemie, 2009. DOI: 10.1002/zaac.200900436