Electronic Supplementary Material (ESI) for CrystEngComm.

The Interesting Fluorine Anion Water Clusters $[F^-\cdot(H_2O)_n]$ in Metal Complex Crystal

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Supporting information

Table of contents

1. Crystallographic data for $[Cd(Im)_6][F\cdot H_2O]_2$

Table 1-1. Crystal data and structure refinement for **$[Cd(Im)_6][F\cdot H_2O]_2$**.

Identification code	qj07113	
Empirical formula	C18 H28 Cd F2 N12 O2	
Formula weight	594.92	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.5545(19) Å	α= 90°.
	b = 16.926(3) Å	β= 90.72(3)°.
	c = 7.8873(16) Å	γ = 90°.
Volume	1275.4(4) $Å^3$	
Z	2	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	0.911 mm^{-1}	
F(000)	604	
Crystal size	0.23 x 0.21 x 0.15 mm^3	
Theta range for data collection	2.132 to 27.918°.	
Index ranges	-11<=h<=12, -17<=k<=22, -9<=l<=10	
Reflections collected	5646	
Independent reflections	2210 [R(int) = 0.0232]	
Completeness to theta = 25.242°	70.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2210 / 0 / 164	
Goodness-of-fit on F^2	0.947	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0617	
R indices (all data)	R1 = 0.0364, wR2 = 0.0661	
Extinction coefficient	0.0305(16)	
Largest diff. peak and hole	0.445 and -0.411 $e.Å^{-3}$	

Table 1-2. Hydrogen bonds for **[Cd(Im)$_6$][F·H$_2$O]$_2$** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O1W#2	0.86	1.91	2.773(3)	179
N4-H4...F1#3	0.86	1.83	2.688(3)	176
N6-H6...F1	0.86	1.80	2.607(3)	156
O1W-H1WA...F1#4	0.85	1.82	2.668(3)	173
O1W-H1WB...F1#5	0.85	1.80	2.619(3)	161

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z-1/2 #3 x,y,z+1

#4 x-1,y,z+1 #5 x-1,-y+1/2,z+3/2

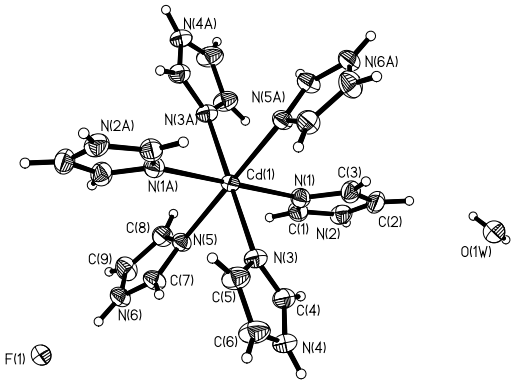

Fig. S1-1 An ORTEP diagram of [Cd(Im)$_6$][F·H$_2$O]$_2$. Atoms with an additional "A" letter in the atom label are at equivalent position (1-x, -y, -z), the percentage probability chosen for the ellipsoids is 30%.

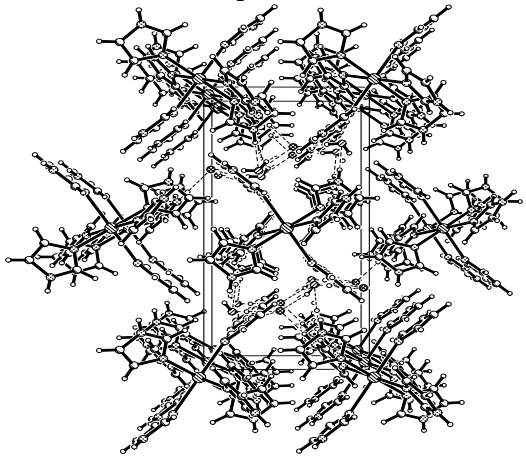

Fig. S1-2 A view of the crystal packing down the *a* axis for [Cd(Im)$_6$][F·H$_2$O]$_2$

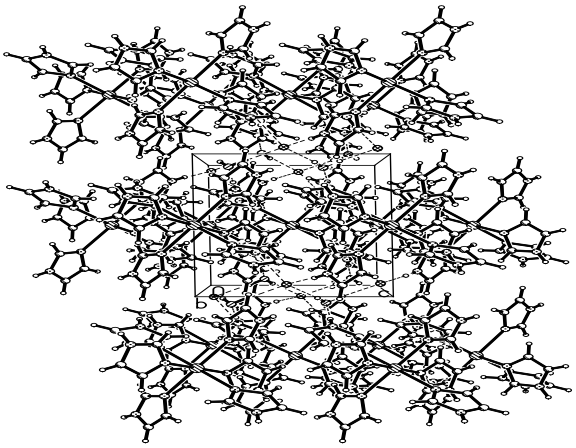

Fig. S1-3 View of the crystal packing down the *b* axis for $[Cd(Im)_6][F\cdot H_2O]_2$

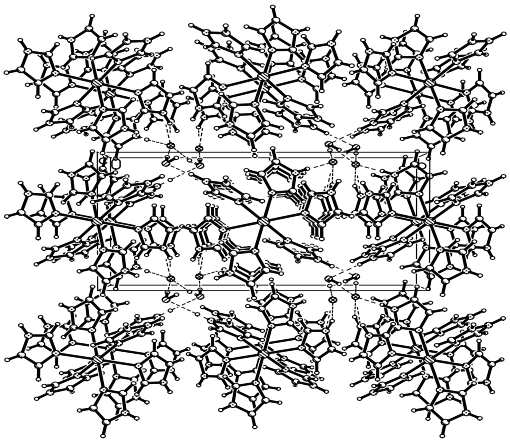

Fig. S1-4 View of the crystal packing down the *c* axis for $[Cd(Im)_6][F\cdot H_2O]_2$

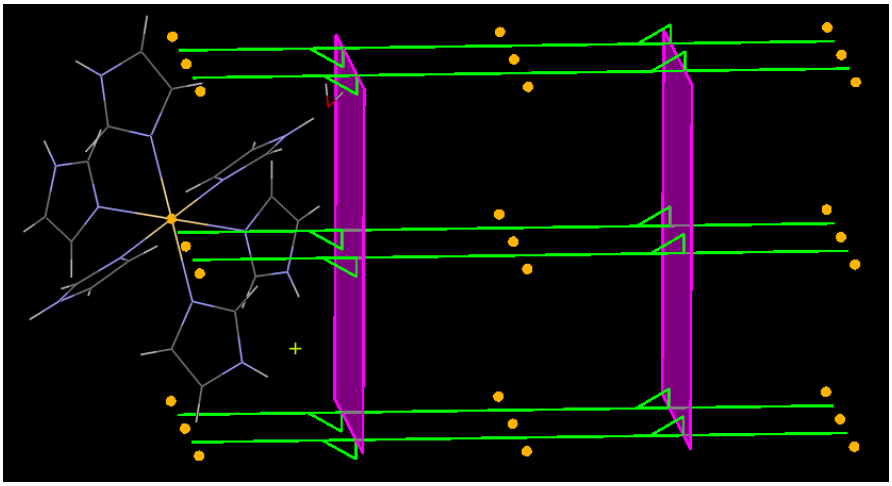

Fig. S1-5 View of Cd atomic position for $[Cd(Im)_6][F\cdot H_2O]_2$

2. Crystallographic data for the $[Ni(Im)_6][F_2 \cdot (H_2O)_5]$

Table 2-1. Crystal data and structure refinement for **$[Ni(Im)_6][F_2 \cdot (H_2O)]$**.

Identification code	qj0794	
Empirical formula	C18 H34 F2 N12 Ni O5	
Formula weight	595.28	
Temperature	293.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 8.9000(18) Å	α= 90°.
	b = 21.140(4) Å	β= 90°.
	c = 15.030(3) Å	γ = 90°.
Volume	2827.8(10) $Å^3$	
Z	4	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	0.750 mm^{-1}	
F(000)	1248	
Crystal size	0.3 x 0.25 x 0.23 mm^3	
Theta range for data collection	1.662 to 28.330°.	
Index ranges	-11<=h<=11, -28<=k<=28, -20<=l<=19	
Reflections collected	36520	
Independent reflections	3569 [R(int) = 0.0254]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3569 / 0 / 185	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0775	
R indices (all data)	R1 = 0.0418, wR2 = 0.0869	
Extinction coefficient	0.0029(4)	
Largest diff. peak and hole	0.198 and -0.248 $e.Å^{-3}$	

Table 2-2. Hydrogen bonds for $[Ni(Im)_6][F_2\cdot(H_2O)]$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...F2#2	0.86	1.80	2.6537(15)	170
N4-H4...F1#3	0.86	1.90	2.7553(15)	177
N6-H6...O1W#3	0.86	1.94	2.7954(16)	179
O1W-H1WA...O5W	0.81	1.87	2.652(2)	162
O1W-H1WB...F2#4	0.84	1.74	2.577(2)	170
O2W-H2WA...F1	0.82	1.87	2.671(2)	164
O2W-H2WB...F1#5	0.88	1.87	2.745(2)	172
O3W-H3WA...F2#4	0.74	2.10	2.840(3)	177
O3W-H3WB...F1#6	0.85	1.96	2.813(3)	178
O4W-H4WA...O2W	0.85	2.01	2.853(3)	173
O4W-H4WB...O3W	0.72	2.19	2.908(3)	174
O5W-H5WA...F2	0.74	2.01	2.756(2)	178
O5W-H5WB...O4W#4	0.83	1.91	2.741(3)	171

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z #2 -x+1,-y,-z #3 x+1/2,y,-z+1/2

#4 x-1/2,y,-z+1/2 #5 x+1/2,y,-z+3/2 #6 x-1/2,y,-z+3/2

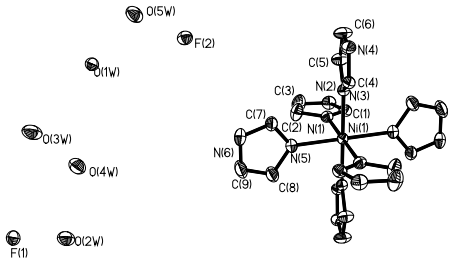

Fig. S2-1 An ORTEP diagram of $[Ni(Im)_6][F_2\cdot(H_2O)_5]$. The percentage probability chosen for the ellipsoids is 30%.

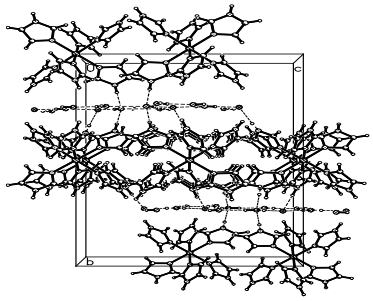

Fig. S2-2 A view of the crystal packing down the *a* axis for $[Ni(Im)_6][F_2\cdot(H_2O)_5]$

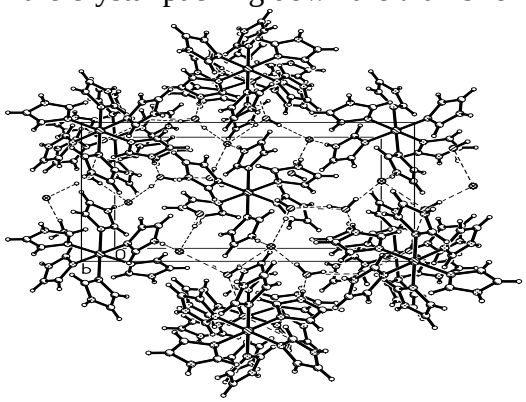

Fig. S2-3 A view of the crystal packing down the *b* axis for $[Ni(Im)_6][F_2\cdot(H_2O)_5]$

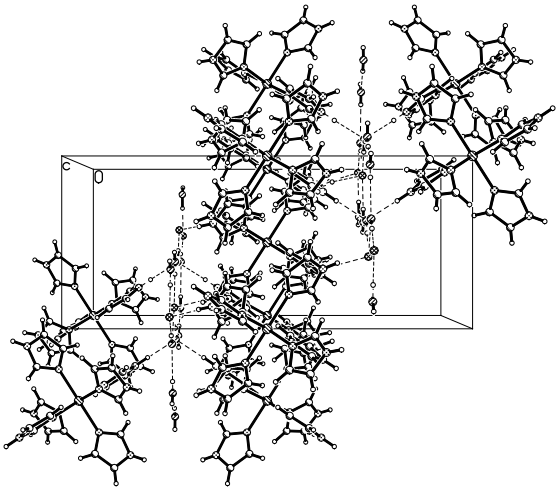

Fig. S2-4 A view of the crystal packing down the *c* axis for $[Ni(Im)_6][F_2\cdot(H_2O)_5]$

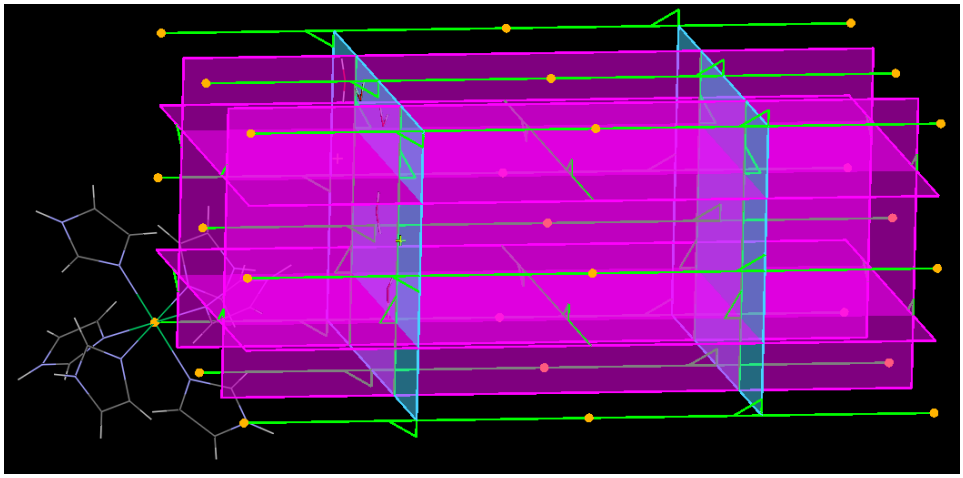

Fig. S2-5 View of Ni atomic position for $[Ni(Im)_6][F_2\cdot(H_2O)_5]$

3. Crystallographic data for the $[Co(Im)_6][F{\cdot}NO_3{\cdot}(H_2O)_4]$

Table 3-1. Crystal data and structure refinement for $[Co(Im)_6][F{\bullet}NO_3{\bullet}(H_2O)_4]$.

Identification code	qj07114	
Empirical formula	C18 H32 Co F N13 O7	
Formula weight	620.49	
Temperature	293.15 K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_3/m$	
Unit cell dimensions	a = 8.9720(13) Å	α= 90°.
	b = 8.9720(13) Å	β= 90°.
	c = 21.077(4) Å	γ = 120°.
Volume	1469.3(5) $Å^3$	
Z	2	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.649 mm^{-1}	
F(000)	646	
Crystal size	0.23 x 0.21 x 0.19 mm^3	
Theta range for data collection	1.932 to 28.240°.	
Index ranges	-11<=h<=11, -11<=k<=9, -26<=l<=28	
Reflections collected	9619	
Independent reflections	1251 [R(int) = 0.0323]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1251 / 0 / 66	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1113	
R indices (all data)	R1 = 0.0542, wR2 = 0.1200	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.331 and -0.668 e.$Å^{-3}$	

Table 3-2. Hydrogen bonds for $[Co(Im)_6][F\cdot NO_3\cdot(H_2O)_4]$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O1#6	0.86	1.90	2.757(2)	173
O2W-H2WB...O1#6	0.85	1.90	2.715(3)	161

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 y,-x+y,-z #3 x-y,x,-z #4 -x+y,-x,z

#5 -y,x-y,z #6 -y+1,x-y,z #7 -x+y+1,-x+1,z

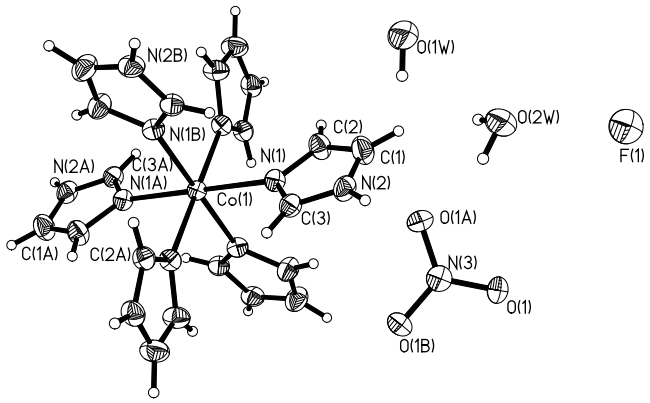

Fig. S3-1 An ORTEP diagram of $[Co(Im)_6][F\cdot NO_3\cdot(H_2O)_4]$. The carbon atoms and nitrogen atoms with an additional "A" letter in the atom label are at equivalent position (-x, -y, -z)，the carbon atoms and nitrogen atoms with an additional "B" letter in the atom label are at equivalent position (-y+x, +x, -z), the oxygen atom with an additional "A" letter in the atom label is at equivalent position (1-y, +x-y, +z), the oxygen atom with an additional "B" letter in the atom label is at equivalent position (1+y-z, 1-x, +z), the percentage probability chosen for the ellipsoids is 30%.

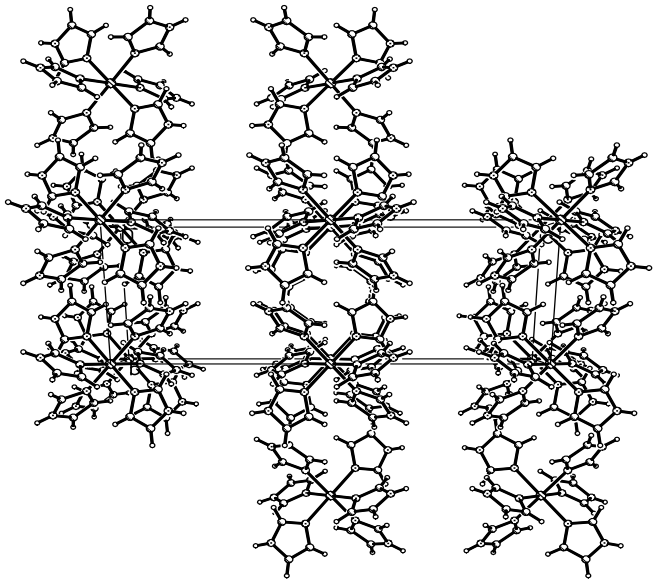

Fig. S3-2 A view of the crystal packing down the *a* axis for $[Co(Im)_6][F{\cdot}NO_3{\cdot}(H_2O)_4]$

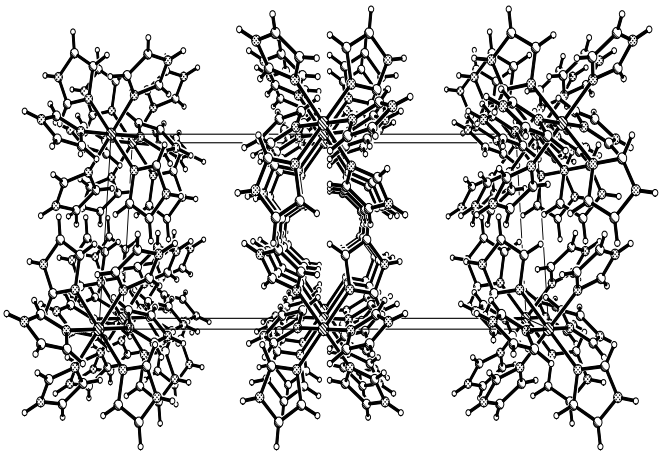

Fig. S3-3 view of the crystal packing down the *b* axis for $[Co(Im)_6][F{\cdot}NO_3{\cdot}(H_2O)_4]$

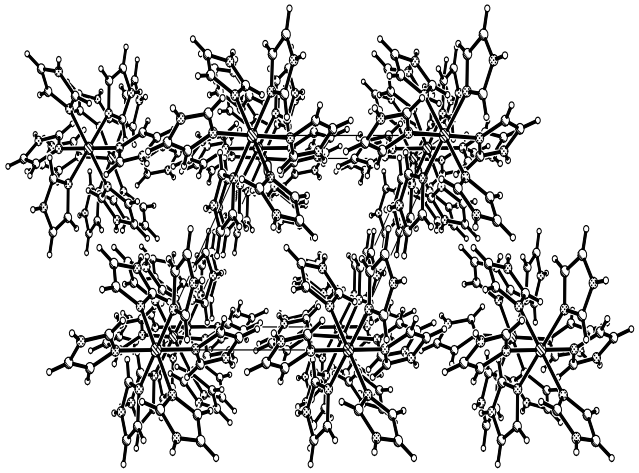

Fig. S3-4 view of the crystal packing down the *c* axis for $[Co(Im)_6][F{\cdot}NO_3{\cdot}(H_2O)_4]$

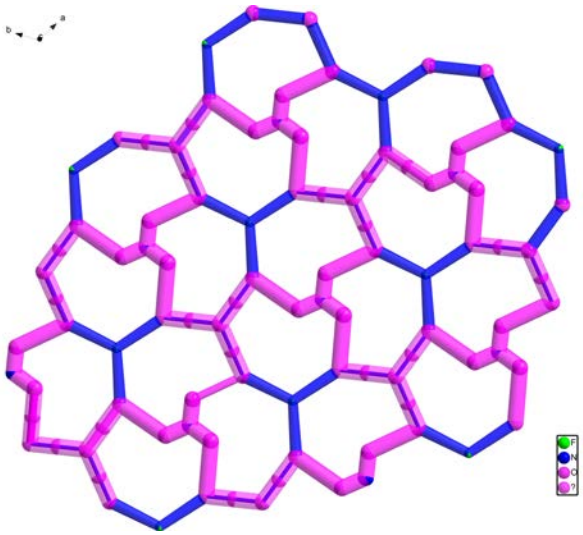

Fig. S3-5 View of $[F^{-}\cdot(H_2O)_4]_n^{n-}$12-membered ring overlap with $[NO_3^{-}\cdot(H_2O)_4]_n^{n-}$ 18-membered ring in the parallel manner

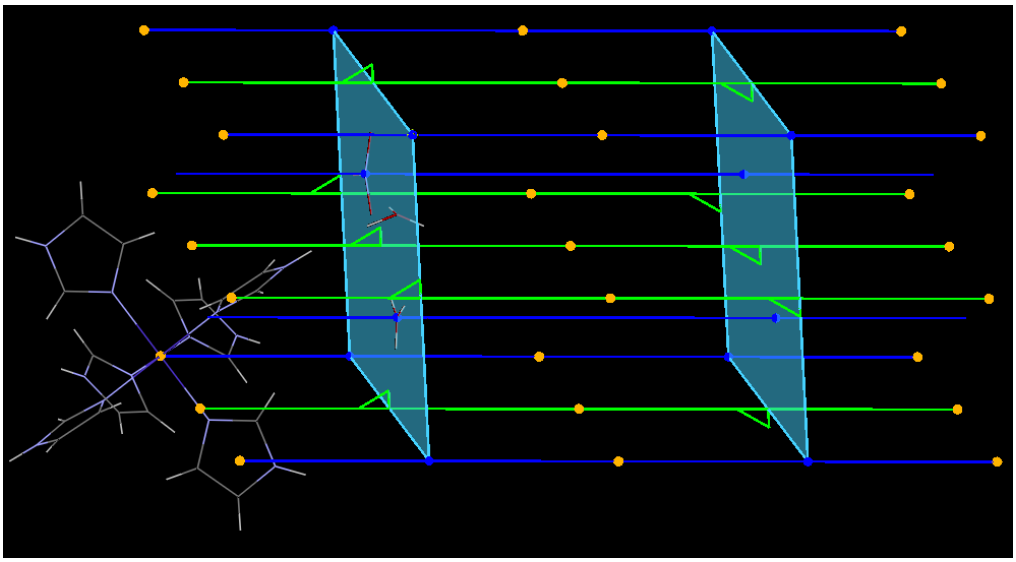

Fig. S3-6 View of Ni atomic position for $[Co(Im)_6][F\cdot NO_3\cdot(H_2O)_4]$.

4. IR spectra

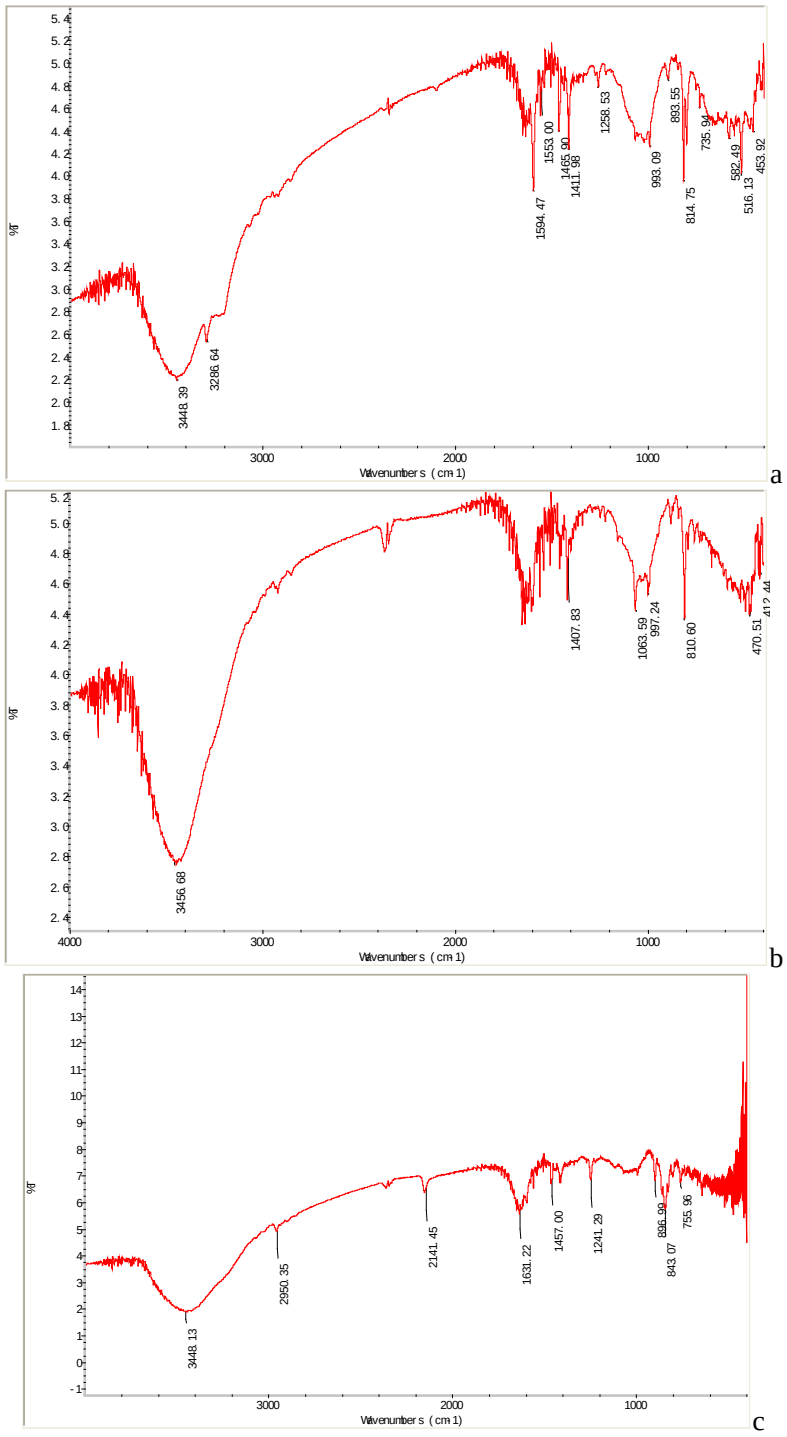

Fig. S4-1 The IR spectra of **(1)**. (a) Sample at 150°C. (b) Sample at 300°C. (c) Sample at 450°C.

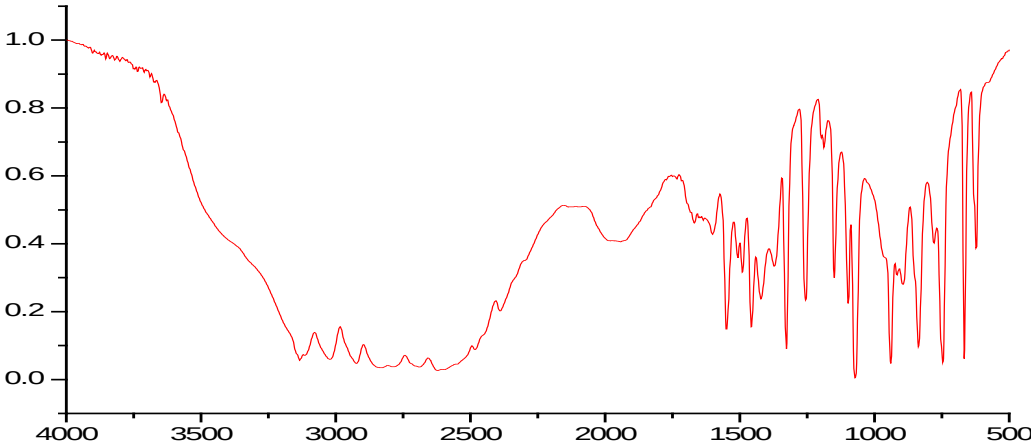

Fig. S4-2 The IR spectra of 2

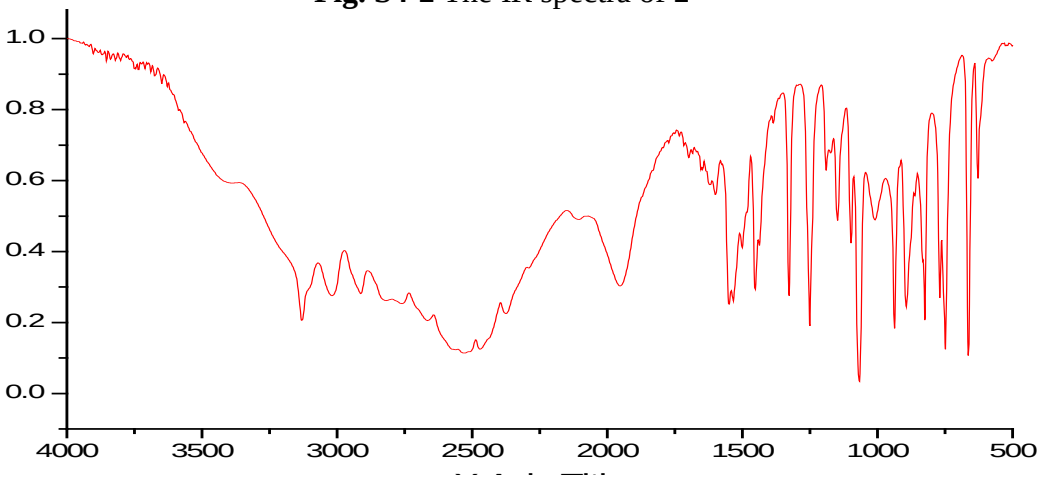

Fig. S4-3 The IR spectra of (**3**)

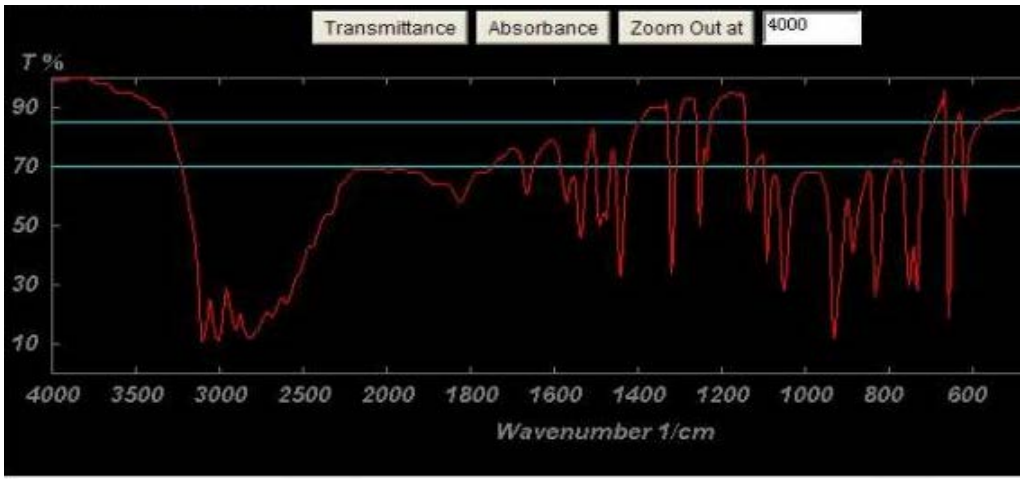

Fig. S4-4 The IR spectra of imidazole

5. Solid State of UV spectra for compounds (1), (2) and (3)

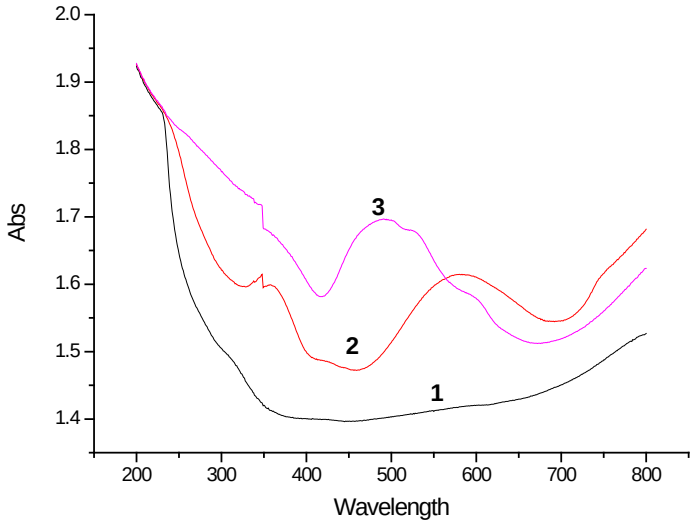

Fig. S5-1 The solid state of UV spectra

6. Solid-state fluorescence

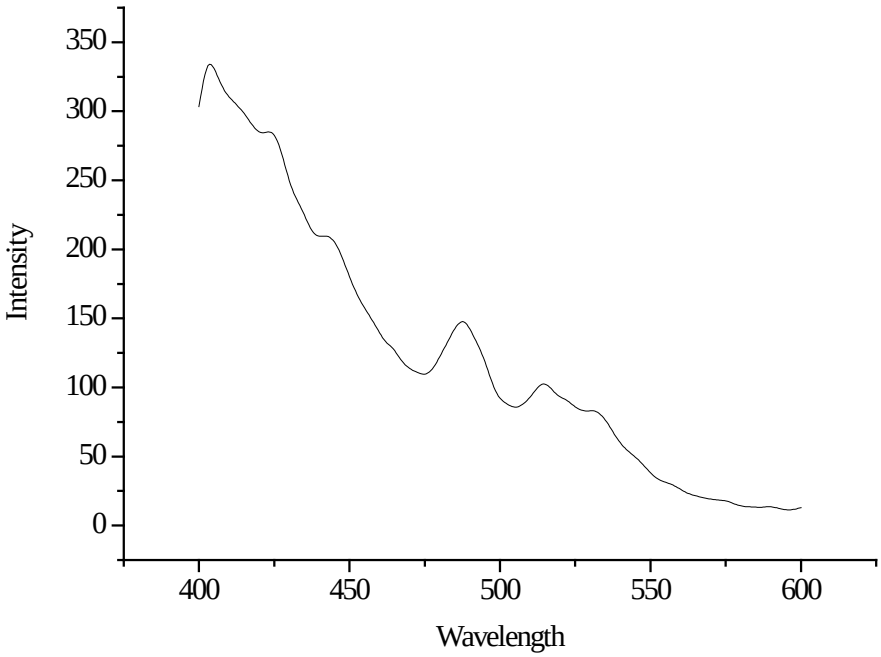

Fig. S6-1 The solid-state fluorescence for compound (**1**).

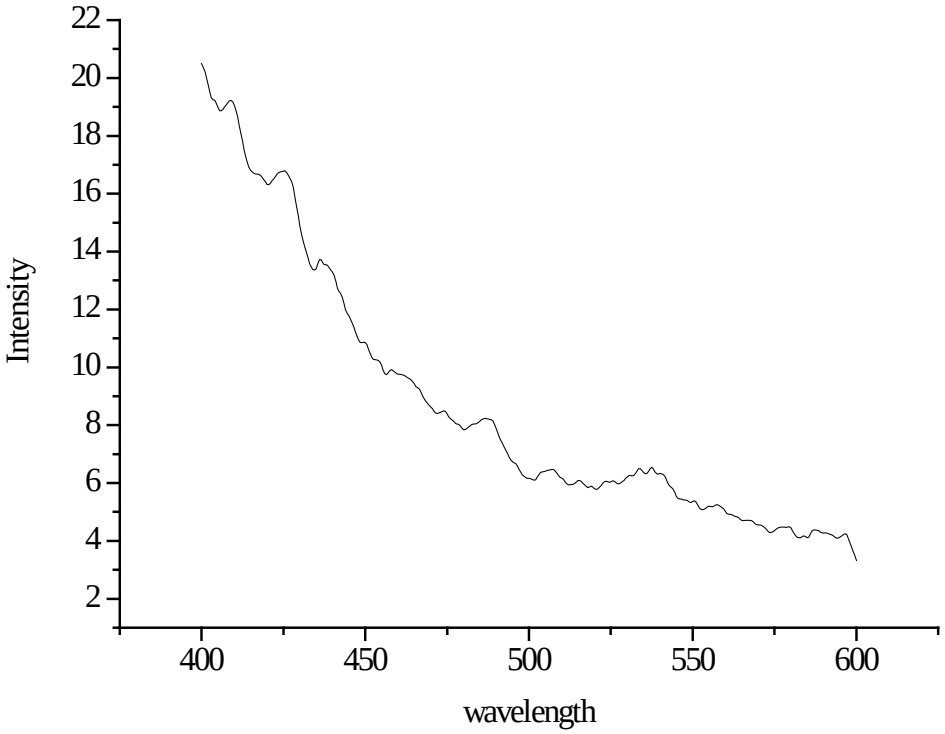

Fig. S6-2 The solid-state fluorescence for compound (**2).**

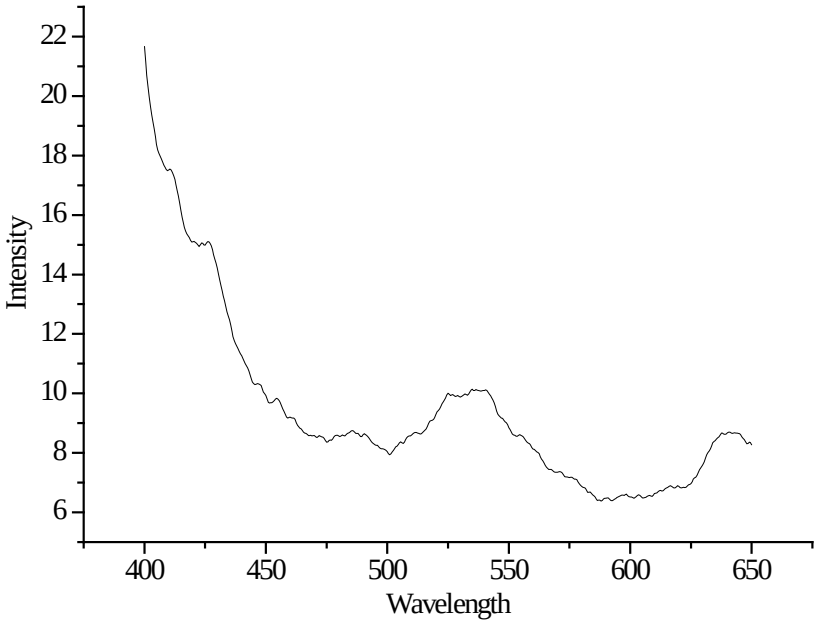

Fig. S6-3 The solid-state fluorescence for compound (**3).**