Structural variations of the first family of heterometallic uranyl carboxyphosphinate assemblies by synergy between carboxyphosphinate and imidazole ligands

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SUPPORTING INFORMATION

I. Tables.

II. Powder X-ray diffraction patterns.

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IV. ORTEP representation of local structures.

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I. Tables.

Table S1 Selected bond lengths (Å) and angles (°) for **1-8**.

1			
U(1)-O(1)#1	1.729(9)	U(2)-O(3)	1.695(9)
U(1)-O(1)	1.729(9)	U(2)-O(2)	1.733(8)
U(1)-O(5)	2.283(9)	U(2)-O(11)#3	2.290(8)
U(1)-O(5)#1	2.283(9)	U(2)-O(4)	2.301(9)
U(1)-O(10)#2	2.299(8)	U(2)-O(6)#4	2.305(9)
U(1)-O(10)#3	2.299(8)	U(2)-O(9)	2.465(9)
		U(2)-O(8)	2.549(9)
Co(1)-O(7)#4	2.078(8)	P(1)-O(4)	1.507(9)
Co(1)-O(7)#5	2.078(8)	P(1)-O(5)	1.516(9)
Co(1)-N(1)#6	2.124(12)	P(1)-C(7)	1.759(13)
Co(1)-N(1)	2.124(12)	P(1)-C(1)	1.779(14)
		P(2)-O(11)	1.504(9)
		P(2)-O(10)	1.517(9)
O(1)#1-U(1)-O(1)	179.998(1)	P(2)-C(10)	1.766(16)
O(3)-U(2)-O(2)	175.3(4)	P(2)-C(16)	1.768(13)
Symmetry codes: #1 -x+2, -y, -z; #2 x, y, z-1; #3 -x+2, -y, -z+1; #4 -x+2, -y+1, -z; #5 x, y, z+1; #6 -x+2, -y+1, -z+1.			
2		**3**	
U(1)-O(1)	1.753(4)	U(1)-O(2)	1.763(7)
U(1)-O(2)	1.753(4)	U(1)-O(1)	1.777(7)
U(1)-O(5)	2.299(3)	U(1)-O(4)	2.276(6)
U(1)-O(6)	2.337(3)	U(1)-O(10)#1	2.307(7)
U(1)-O(7)	2.400(3)	U(1)-O(8)#2	2.312(6)
U(1)-O(4)	2.443(3)	U(1)-O(6)#1	2.464(7)
U(1)-O(3)	2.498(3)	U(1)-O(5)#1	2.526(6)
Zn(1)-O(8)	1.925(3)	Cd(1)-O(7)#3	2.228(7)
Zn(1)-O(9)	1.935(3)	Cd(1)-N(3)#4	2.238(8)
Zn(1)-O(10)#1	1.951(3)	Cd(1)-O(3)#5	2.266(6)
Zn(1)-N(1)	1.974(4)	Cd(1)-N(1)	2.290(8)
		Cd(1)-O(9)	2.384(7)
		Cd(1)-O(5)	2.512(7)
P(1)-O(8)	1.509(3)	P(1)-O(3)	1.482(7)
P(1)-O(6)	1.516(4)	P(1)-O(4)	1.523(7)
P(1)-C(3)	1.783(5)	P(1)-C(1)	1.779(12)
P(1)-C(4)	1.795(5)	P(1)-C(7)	1.786(10)
P(2)-O(5)	1.493(4)	P(2)-O(7)	1.483(7)
P(2)-O(9)	1.500(4)	P(2)-O(8)	1.519(7)
P(2)-C(12)	1.793(5)	P(2)-C(16)	1.787(10)
P(2)-C(13)	1.793(6)	P(2)-C(10)	1.793(13)
O(1)-U(1)-O(2)	178.75(17)	O(2)-U(1)-O(1)	178.3(3)

Symmetry codes: #1 x, y+1, z for **2**; #1 -x+1, -y, -z+1; #2 x, y, z-1; #3 -x, -y, -z+2; #4 x+1, y-1, z; #5 -x, -y, -z+1 for **3**.

4		**5**	
U(1)-O(2)	1.760(5)	U(1)-O(1)	1.742(7)
U(1)-O(1)	1.769(5)	U(1)-O(2)	1.743(7)
U(1)-O(13)#1	2.259(4)	U(1)-O(13)#1	2.277(6)
U(1)-O(3)	2.275(5)	U(1)-O(3)	2.274(6)
U(1)-O(4)	2.300(4)	U(1)-O(4)	2.277(6)
U(1)-O(5)	2.277(5)	U(1)-O(5)	2.284(6)
U(2)-O(7)	1.747(5)	U(2)-O(7)	1.744(8)
U(2)-O(8)	1.750(5)	U(2)-O(8)	1.749(7)
U(2)-O(11)#1	2.296(5)	U(2)-O(11)#1	2.266(7)
U(2)-O(9)	2.313(4)	U(2)-O(9)	2.310(6)
U(2)-O(6)#1	2.329(5)	U(2)-O(6)#1	2.326(7)
U(2)-O(15)#2	2.469(5)	U(2)-O(15)#2	2.454(8)
U(2)-O(16)#2	2.482(5)	U(2)-O(16)#2	2.504(7)
Cd(1)-O(14)	2.215(5)	Mn(1)-O(14)	2.078(7)
Cd(1)-O(10)#3	2.293(5)	Mn(1)-O(10)#3	2.161(8)
Cd(1)-O(12)	2.324(5)	Mn(1)-O(12)	2.180(7)
Cd(1)-N(3)	2.245(6)	Mn(1)-N(3)	2.184(9)
Cd(1)-N(1)	2.254(6)	Mn(1)-N(1)	2.212(9)
P(1)-O(5)	1.510(5)	P(1)-O(5)	1.515(7)
P(1)-O(6)	1.514(5)	P(1)-O(6)	1.513(7)
P(1)-C(1)	1.813(8)	P(1)-C(1)	1.771(11)
P(1)-C(7)	1.768(7)	P(1)-C(7)	1.794(9)
P(2)-O(14)	1.475(5)	P(2)-O(14)	1.480(7)
P(2)-O(3)	1.509(5)	P(2)-O(3)	1.522(6)
P(2)-C(10)	1.787(8)	P(2)-C(11)	1.771(12)
P(2)-C(16)	1.811(7)	P(2)-C(17)	1.835(15)
P(3)-O(9)	1.493(5)	P(3)-O(9)	1.501(7)
P(3)-O(4)	1.509(5)	P(3)-O(4)	1.528(7)
P(3)-C(25)	1.792(7)	P(3)-C(27)	1.780(10)
P(3)-C(19)	1.799(7)	P(3)-C(21)	1.783(11)
O(2)-U(1)-O(1)	178.2(2)	O(1)-U(1)-O(2)	178.4(3)
O(7)-U(2)-O(8)	177.3(2)	O(7)-U(2)-O(8)	177.0(4)

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

	6 (Co)	**7** (Ni)	**8** (Cu)
U(1)-O(1)#1	1.774(6)	1.769(5)	1.775(5)
U(1)-O(1)	1.774(6)	1.769(5)	1.775(5)
U(1)-O(11)#2	2.256(6)	2.262(4)	2.258(4)
U(1)-O(11)#3	2.256(6)	2.262(4)	2.258(4)
U(1)-O(4)	2.279(5)	2.285(4)	2.288(5)
U(1)-O(4)#1	2.279(5)	2.285(4)	2.288(5)
U(2)-O(2)	1.769(6)	1.762(5)	1.764(5)

U(2)-O(3)	1.776(6)	1.768(5)	1.771(5)
U(2)-O(8)	2.299(6)	2.296(4)	2.305(4)
U(2)-O(10)#4	2.317(5)	2.326(4)	2.312(5)
U(2)-O(5)#5	2.322(6)	2.327(4)	2.335(4)
U(2)-O(7)	2.441(6)	2.437(5)	2.442(5)
U(2)-O(6)	2.507(5)	2.506(4)	2.507(5)
M(1)-N(1)	2.122(6)	2.075(5)	1.993(5)
M(1)-N(1)#6	2.122(6)	2.075(5)	1.993(5)
M(1)-N(3)	2.153(7)	2.121(5)	2.046(5)
M(1)-N(3)#6	2.153(7)	2.121(5)	2.046(5)
M(1)-O(1W)	2.137(6)	2.116(5)	2.502(6)
M(1)-O(1W)#6	2.137(6)	2.116(5)	2.502(6)
P(1)-O(5)	1.505(6)	1.505(4)	1.503(5)
P(1)-O(4)	1.518(5)	1.513(5)	1.522(5)
P(1)-C(7)	1.781(8)	1.780(7)	1.782(8)
P(1)-C(1)	1.803(9)	1.795(8)	1.796(8)
P(2)-O(10)	1.516(5)	1.508(4)	1.511(5)
P(2)-O(11)	1.523(6)	1.522(4)	1.520(4)
P(2)-C(16)	1.777(9)	1.782(7)	1.783(8)
P(2)-C(10)	1.795(9)	1.789(7)	1.789(7)
O(1)#1-U(1)-O(1)	180.000(1)	180.000(1)	180.0(6)
O(2)-U(2)-O(3)	178.4(3)	178.3(2)	178.1(2)

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

Table S2 Average bond lengths of six-fold and seven-fold coordinated uranium cations in **1-8**.

	Six-fold coordinated U cations		Seven-fold coordinated U cations	
	U=O (Å)	U-O (Å)	U=O (Å)	U-O (Å)
1	1.729	2.291	1.715	2.383
2	--	--	1.753	2.396
3	--	--	1.771	2.378
4	1.765	2.278	1.749	2.378
5	1.743	2.279	1.747	2.373
6	1.775	2.268	1.773	2.378
7	1.770	2.274	1.766	2.379
8	1.776	2.273	1.768	2.381

Table S3 IR spectroscopic data for **1-8**.

	C-H (aromatic ring)/cm^{-1}	C=C, C-N, COO / cm^{-1}	O=U=O /cm^{-1}	O−P−O, P−C /cm^{-1}
1		1563, 1524, 1434, 1406, 1310	960, 930, 919, 844	1088, 1041, 742, 695
2	3057	1554, 1526, 1489, 1432, 1404, 1320	948, 918, 839	1100, 1030, 750, 690
3	3131	1590, 1519, 1444, 1404, 1312	948, 909, 856	1100, 1052, 742, 698
4	3131	1584, 1519, 1440, 1380, 1311	949, 938, 901, 856	1100, 1011, 723, 698
5	3137	1569, 1525, 1440, 1405, 1310	932, 903, 839	1057, 1022, 729, 701
6	3136	1590, 1529, 1435, 1384, 1313	934, 900, 845	1099, 1016,743, 691
7	3136	1590, 1524, 1435, 1310	936, 904, 841	1100, 1011, 743, 692
8		1529, 1454, 1407, 1313	920, 840	1100, 1042, 770, 733, 690

Table S4 Comparison of selected single-crystal XRD and IR spectroscopic data for **1-8** using Veal's empirical law $R_{U-O}(pm) = 8120\nu_3^{-2/3} + 89.5$.

	ν_3 (cm^{-1}) in IR	Calculate from IR (pm)	Single XRD data (pm)
1	960, 929.7, 919	172.7, 174.7, 175.4,	169.5, 172.9, 173.3
2	948, 918	173.6, 175.5	175.3
3	948, 909, 856	173.6, 176.0, 179.6	176.3, 177.7
4	948.9, 938.4, 901	173.6, 174.2, 176.5	174.7, 175.0, 176.0, 176.9
5	932, 902.5	174.6, 176.4	174.2, 174.3, 174.4
6	934.3, 900	174.5, 176.6	176.9, 177.4, 177.6
7	936.3, 904	174.3, 176.4	176.2, 176.8, 176.9
8	919.7	175.4,	176.4, 177.1, 177.5

II. Powder X-ray diffraction patterns.

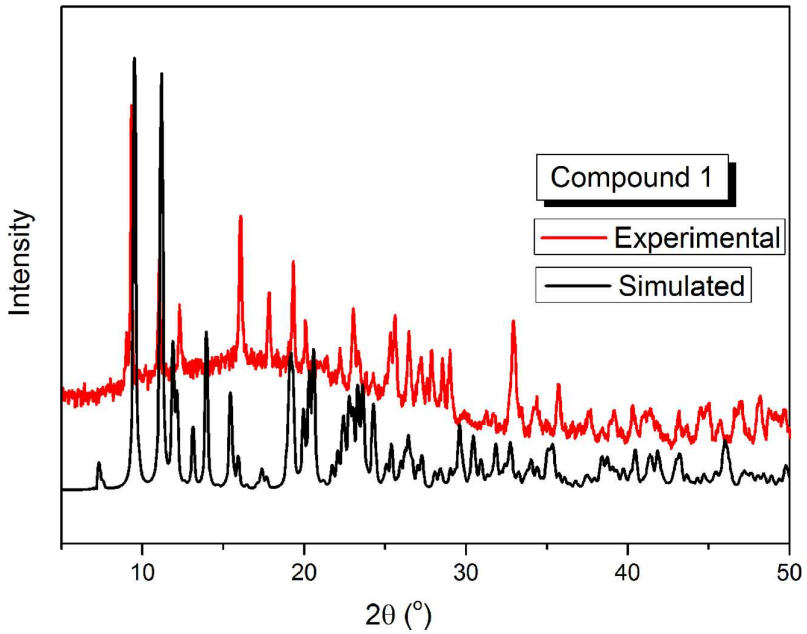

Figure S1. PXRD pattern of $Co(im)_2(UO_2)_3(L)_4$ **1**.

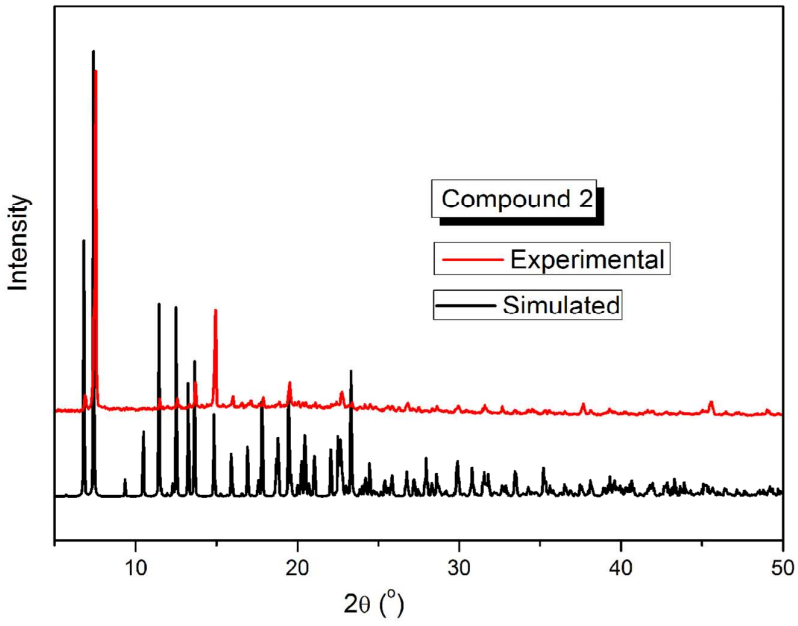

Figure S2. PXRD pattern of $Zn(bpi)(UO_2)(L)_2$ **2**.

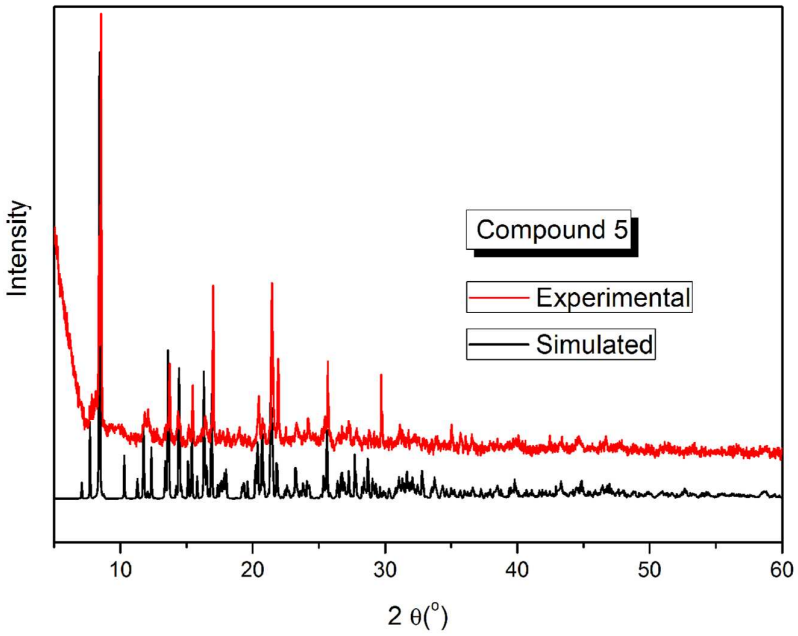

Figure S3. PXRD pattern of $Mn(dib)(UO_2)_2(L)_3$ **5**.

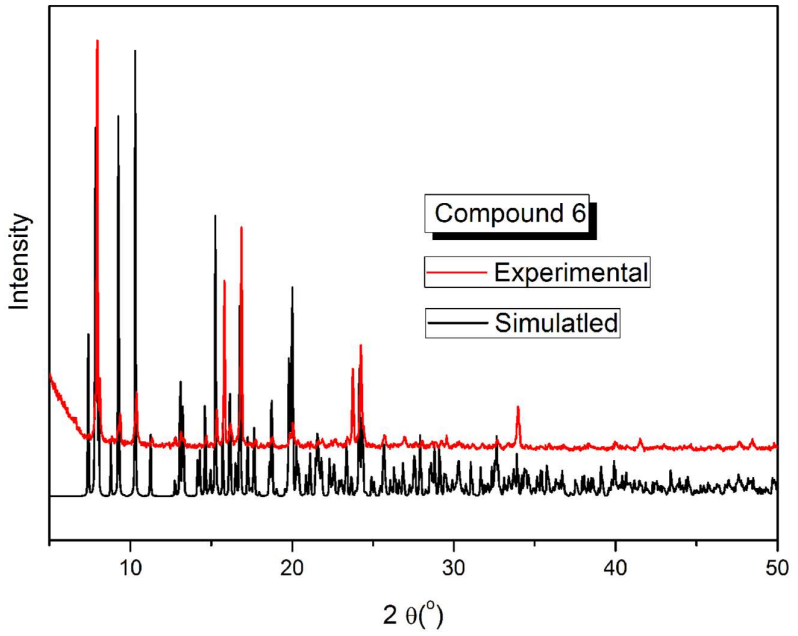

Figure S4. PXRD pattern of $[Co(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **6**.

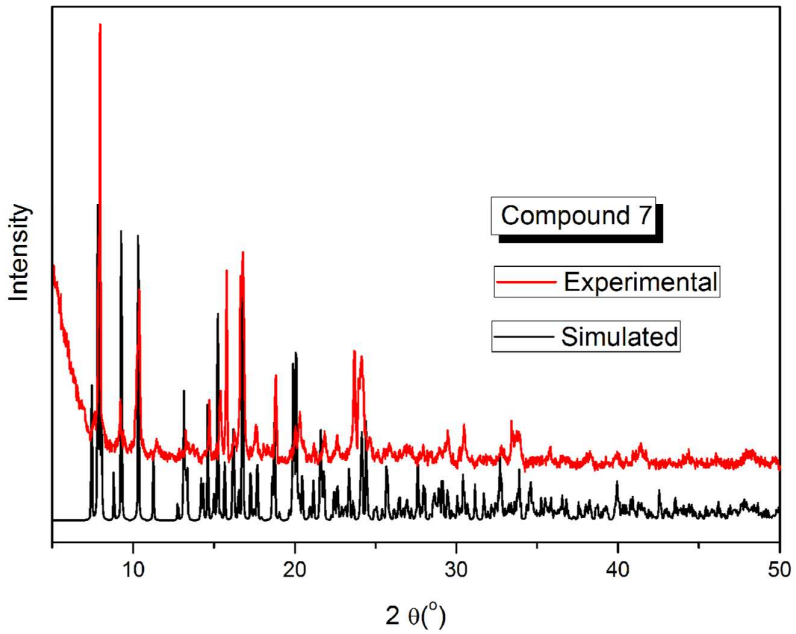

Figure S5. PXRD pattern of $[Ni(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **7**.

III. Infrared spectra

The strong peaks from 960 to 900 cm^{-1} are ascribed to the antisymmetric stretching modes v_3 of uranyl dication; whilst those in the range of 839-812 cm^{-1} are due to the symmetric stretching vibrations v_1. The bands in the range from 1100 to 1000 cm^{-1} and in the low wavenumber region from 750 to 690 cm^{-1} are dominated by the O−P−O bending and P−C stretching vibrations. The vibrations of the aromatic rings are indicated in the area 1590-1310 cm^{-1}. The peak located at 3130 cm^{-1} is attributed to the C-H stretching vibrations of the aromatic ring.

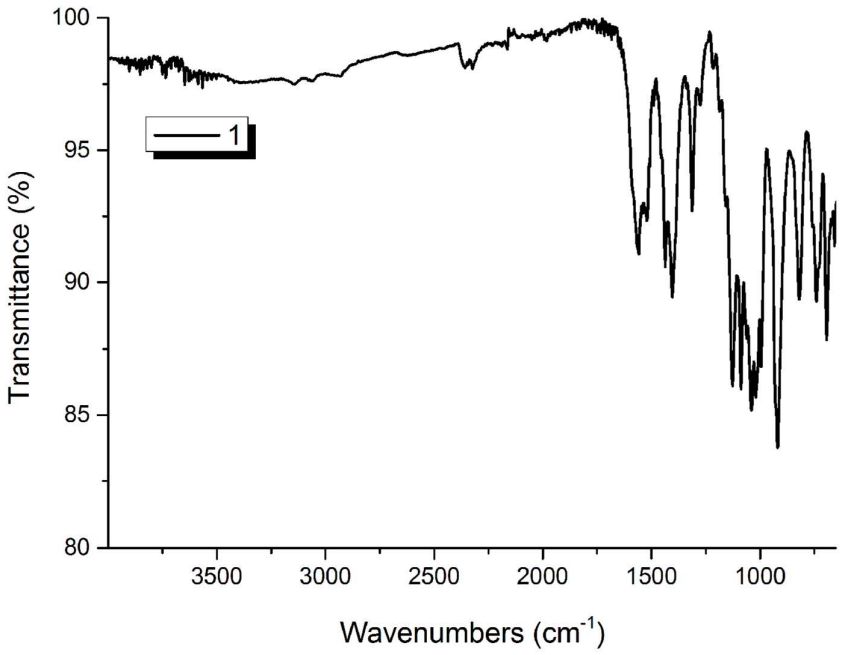

Figure S6. IR spectrum of $Co(im)_2(UO_2)_3(L)_4$ **1**.

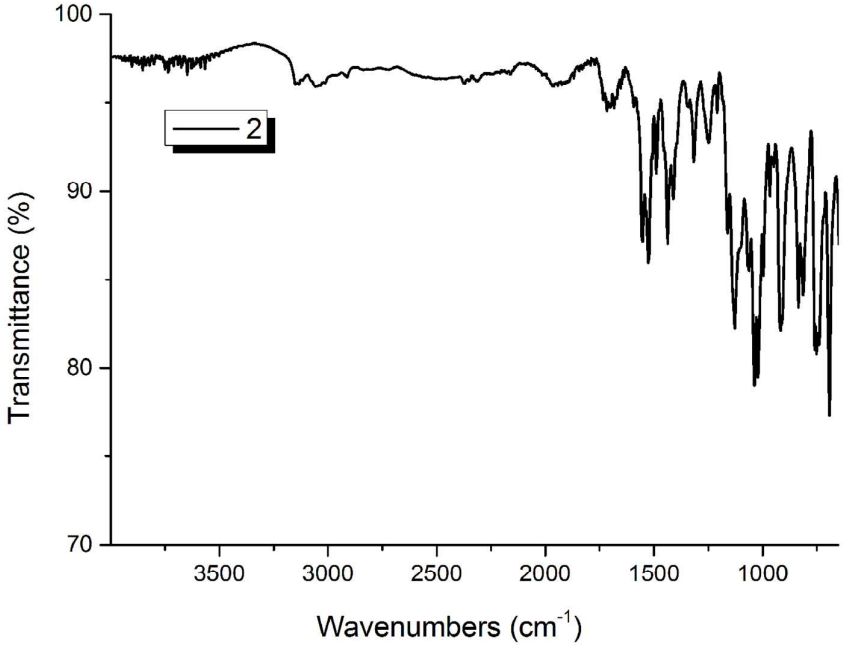

Figure S7. IR spectrum of $Zn(bpi)(UO_2)(L)_2$ **2**.

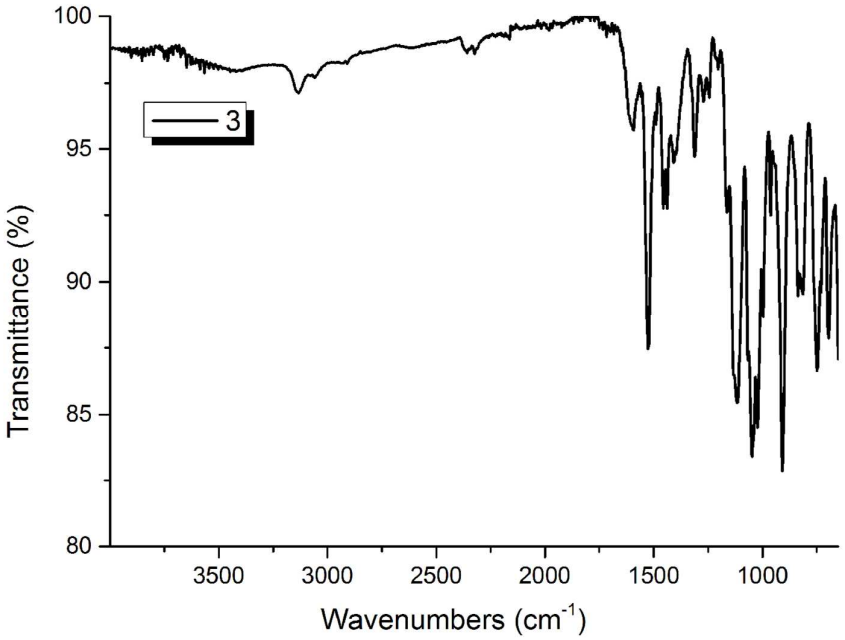

Figure S8. IR spectrum of Cd(dib)(UO_2)(L)$_2$ **3**.

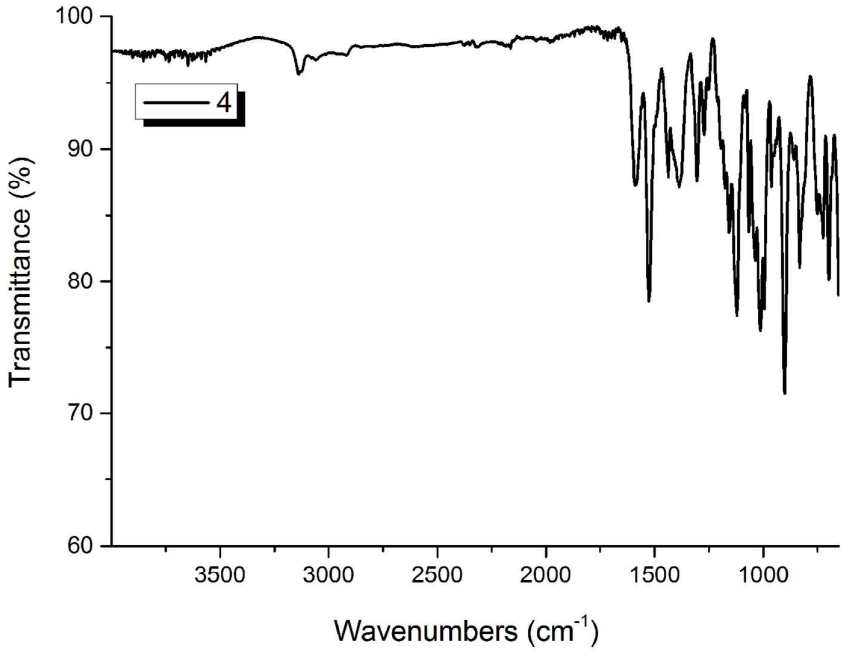

Figure S9. IR spectrum of Cd(dib)(UO_2)$_2$(L)$_3$ **4**.

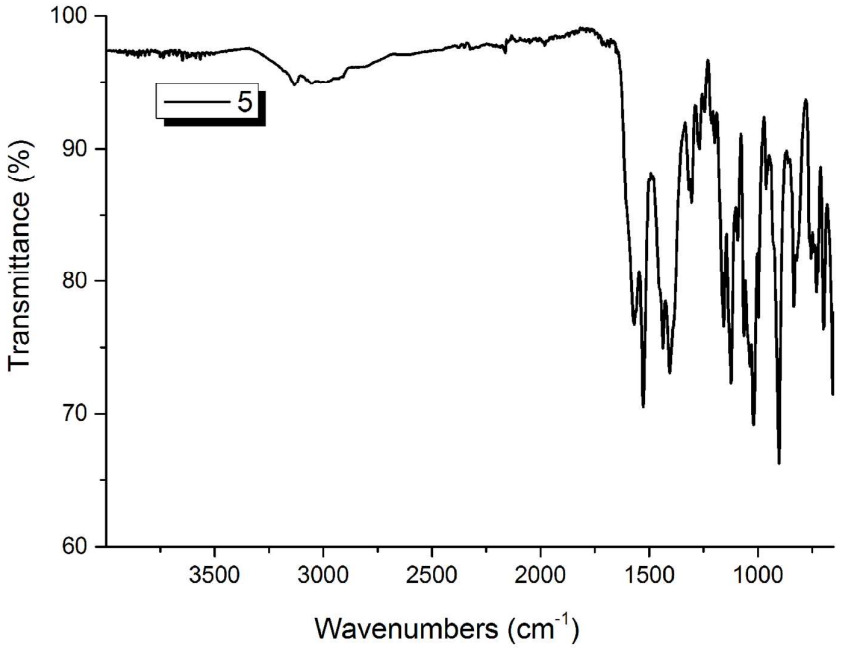

Figure S10. IR spectrum of $Mn(dib)(UO_2)_2(L)_3$ **5**.

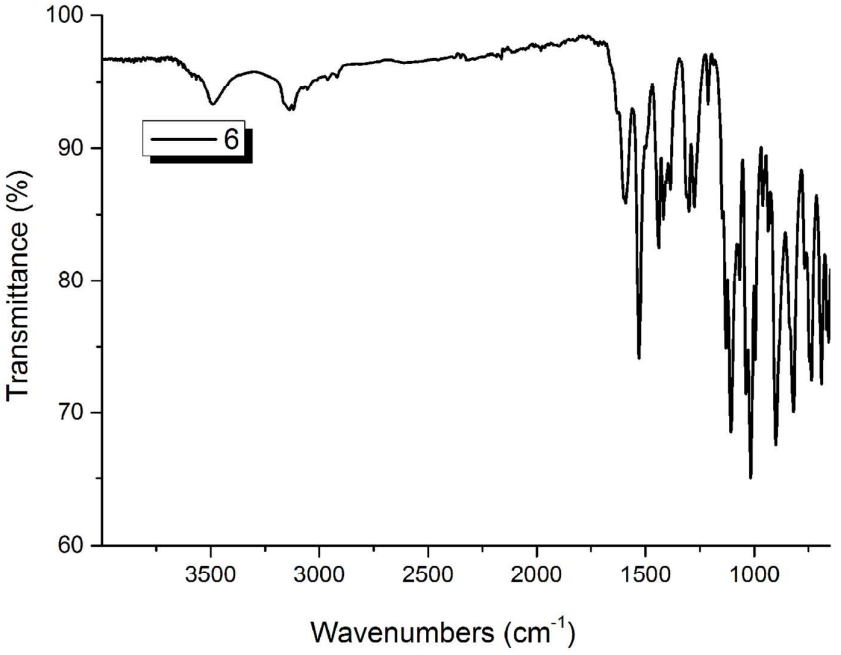

Figure S11. IR spectrum of $[Co(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **6**.

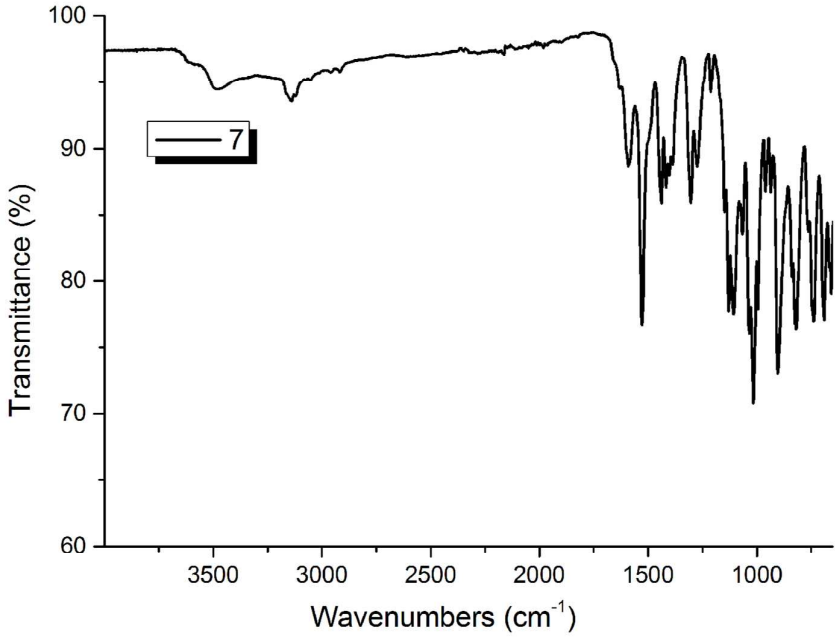

Figure S12. IR spectrum of $[Ni(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **7**.

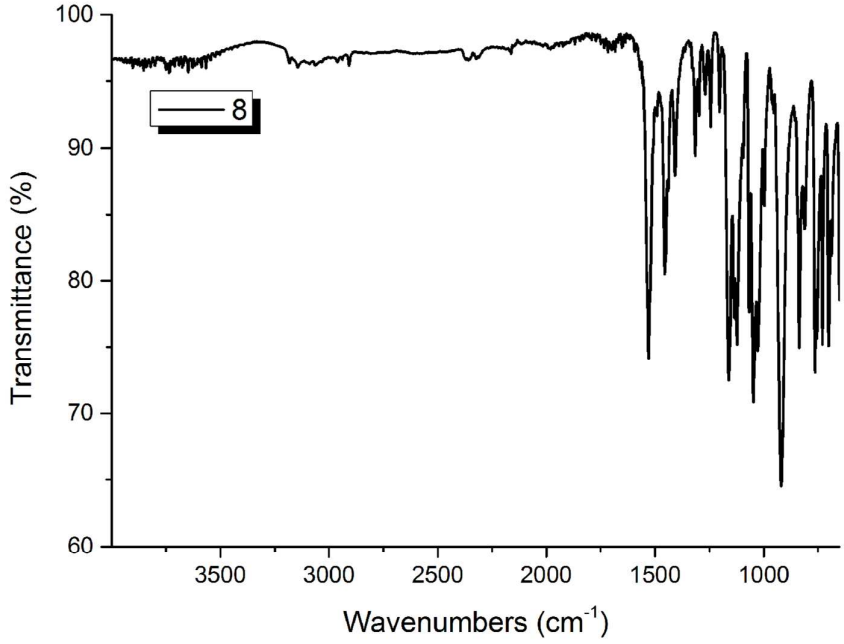

Figure S13. IR spectrum of $[Cu(dib)_2(H_2O)_2][(UO_2)_3(L)_4]$ **8**.

IV. ORTEP representation of local structures.

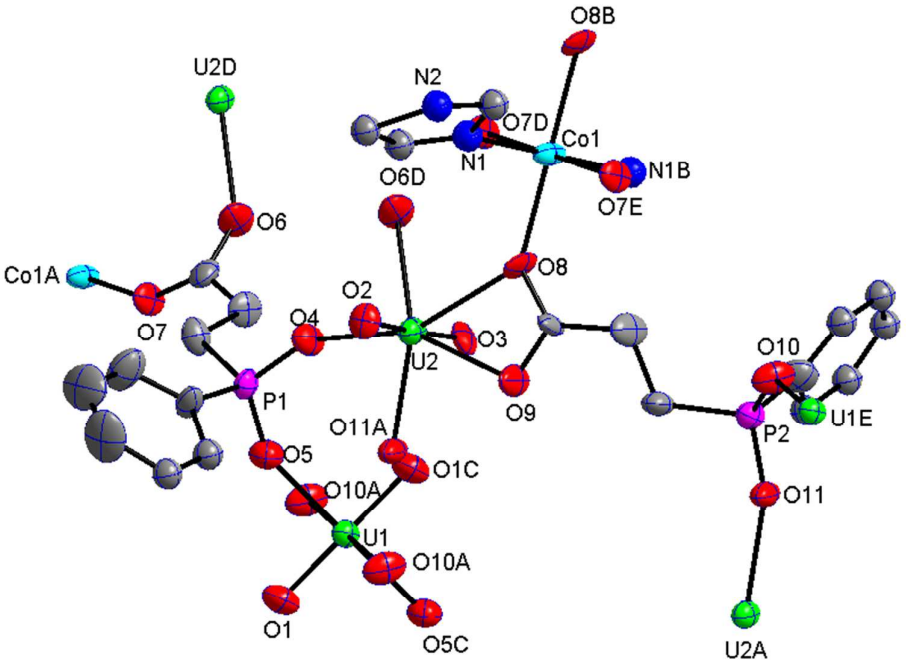

Figure S14. ORTEP representation of local structure of $Co(im)_2(UO_2)_3(L)_4$ **1**. Symmetry codes: A, 2-x, -y, 1-z; B, 2-x, 1-y, 1-z; C, 2-x, -y, -z; D, 2-x, 1-y, -z; E, x, y, 1+z.

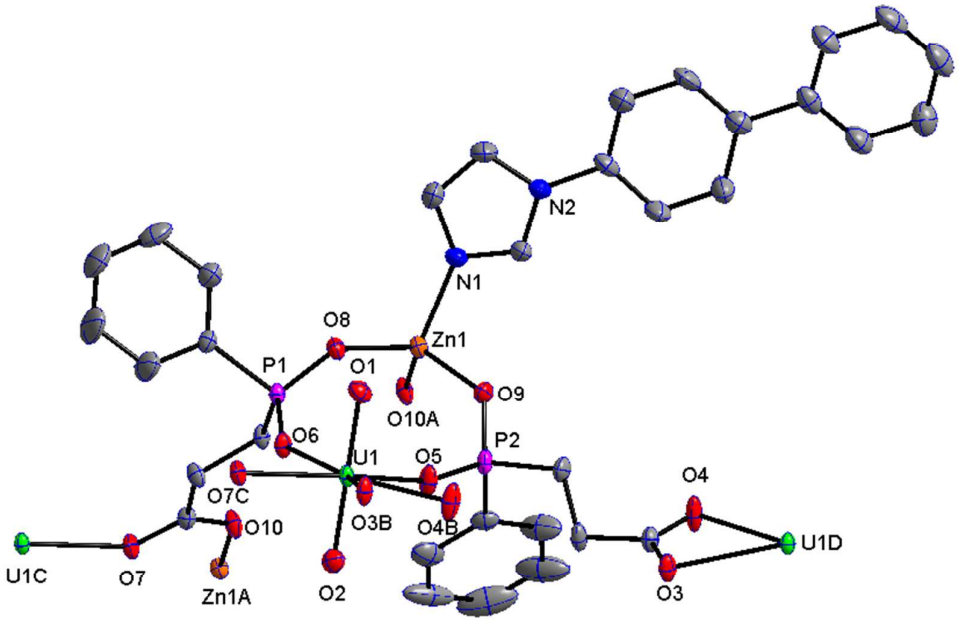

Figure S15. ORTEP representation of local structure of $Zn(bpi)(UO_2)(L)_2$ **2**. Symmetry codes: A, 1-x, 2-y, 1-z; B, 1-x, 0.5+y, 1.5-z; C, 1-x, 3-y, 1-z; D, 1-x, -0.5+y, 1.5-z.

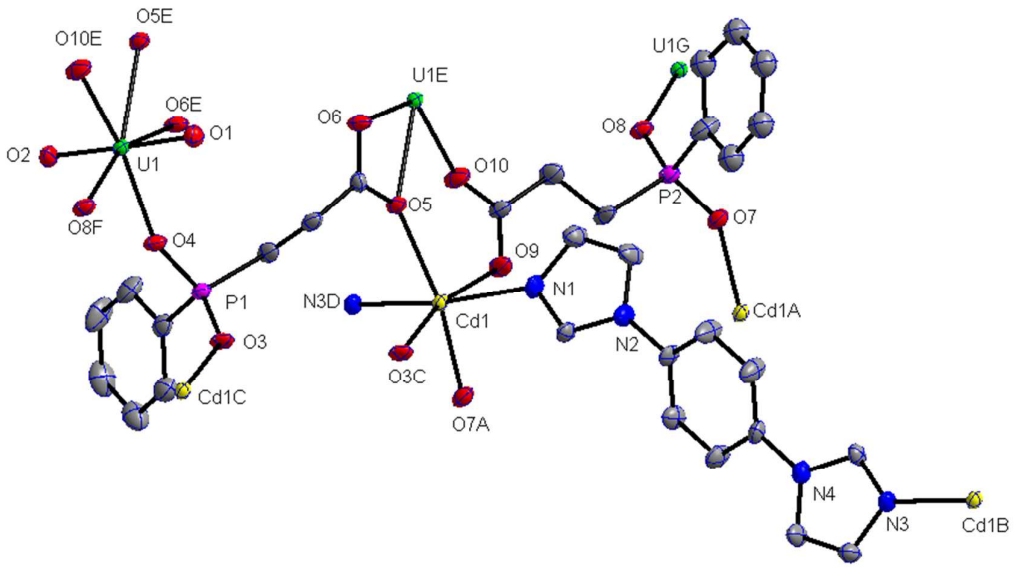

Figure S16. ORTEP representation of local structure of $Cd(dib)(UO_2)(L)_2$ **3**. Symmetry codes: A, -x, -y, 2-z; B, -1+x, 1+y, z; C, -x, -y, 1-z; D, 1+x, -1+y, z; E, 1-x, -y, 1-z; F, x, y, -1+z; G, x, y, 1+z.

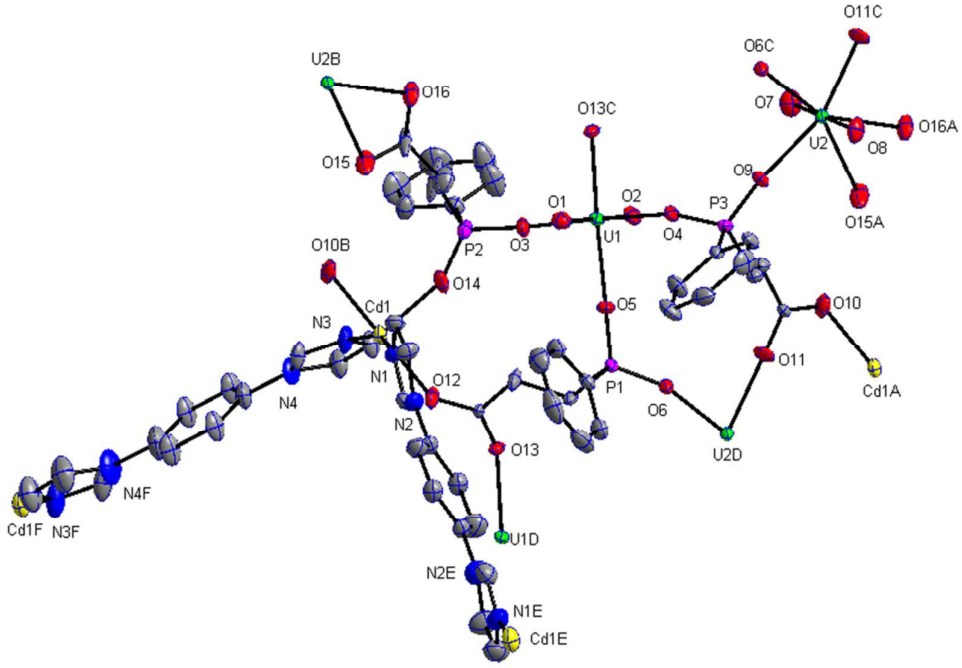

Figure S17. ORTEP representation of local structure of $Cd(dib)(UO_2)_2(L)_3$ **4.** Symmetry codes: A, x, 1+y, z; B, x, -1+y, z; C, -1+x, y, z; D, 1+x, y, z; E, 2-x, -y, 1-z; F, 2-x, -1-y, -z.

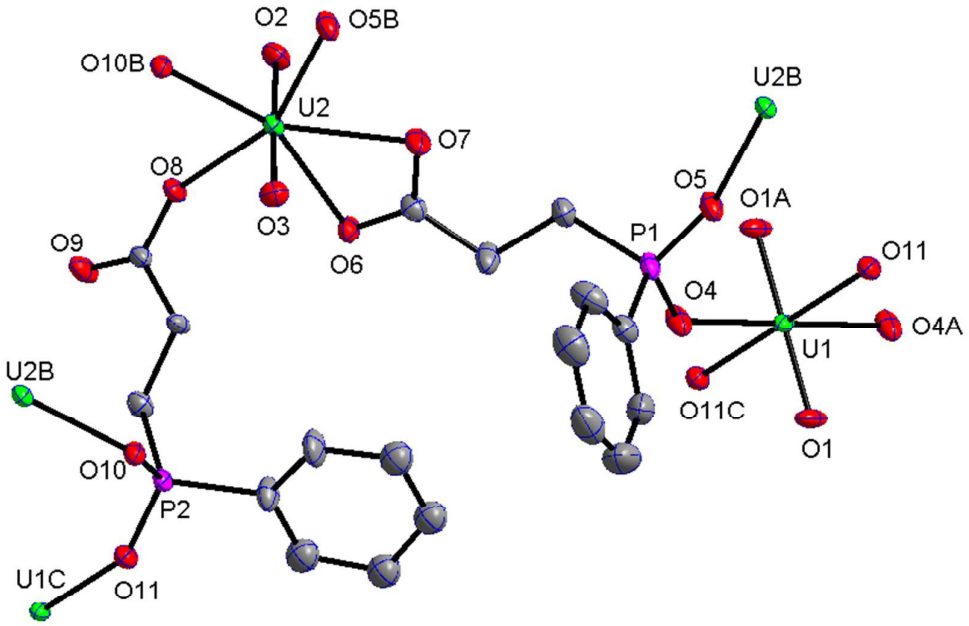

Figure S18. ORTEP representation of local structure of $[Co(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **6**. Symmetry codes: A, 1-x, 1-y, 1-z; B, 1-x, -y, 1-z; C, x, y, -1+z.

V. Excitation and Emission spectra.

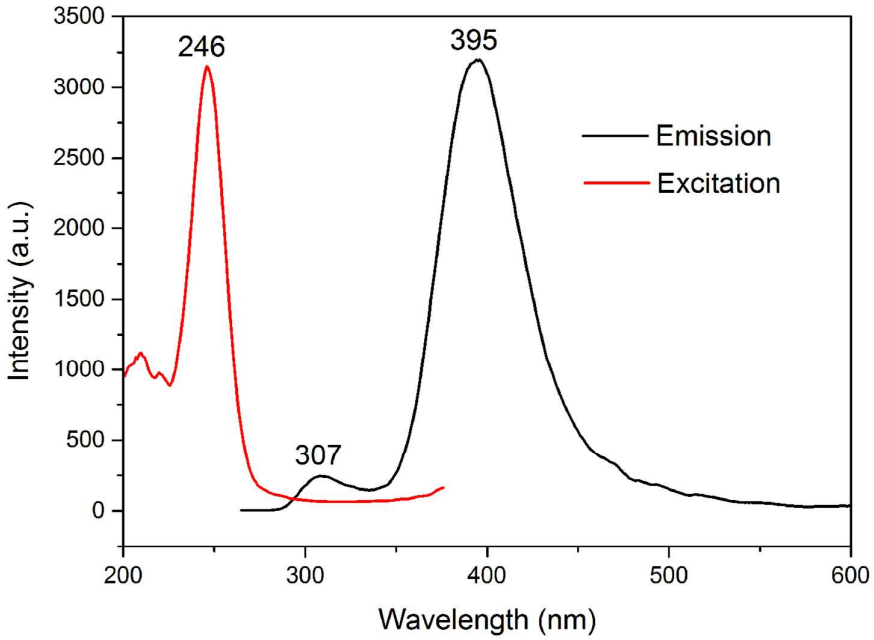

Figure S19. Excitation and emission spectra of $Co(im)_2(UO_2)_3(L)_4$ **1**.

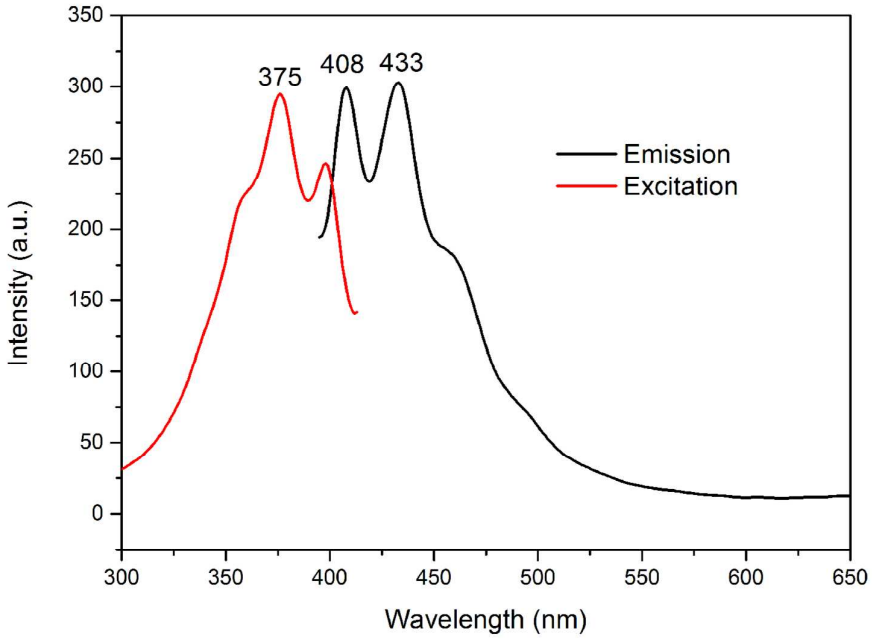

Figure S20. Excitation and emission spectra of $Mn(dib)(UO_2)_2(L)_3$ **5**.

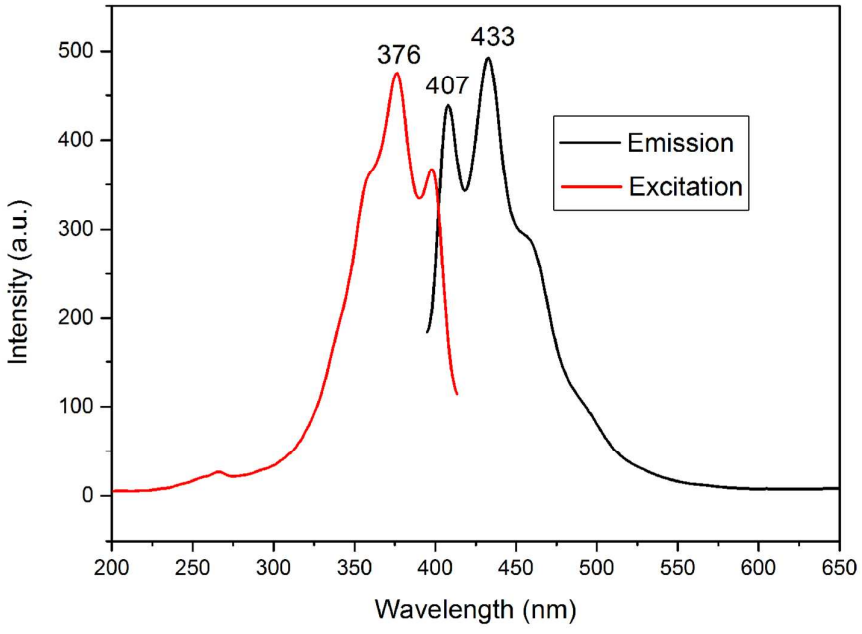

Figure S21. Excitation and emission spectra of $[Co(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **6**.

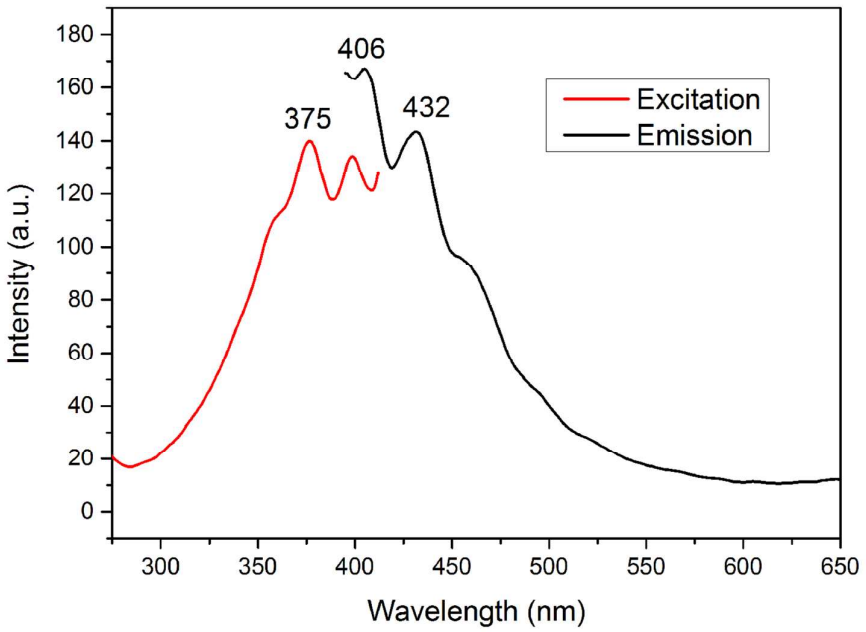

Figure S22. Excitation and emission spectra of $[Ni(dib)_2(H_2O)_2][(UO_2)_3(L)_4]\cdot 2H_2O$ **7.**

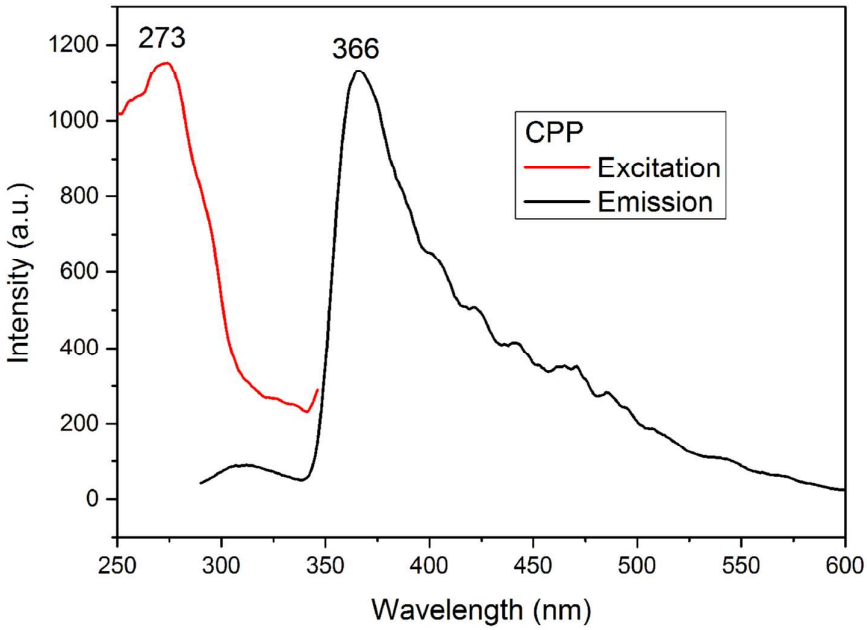

Figure S23. Excitation and emission spectra of the carboxphosphinate ligand **CPP**.

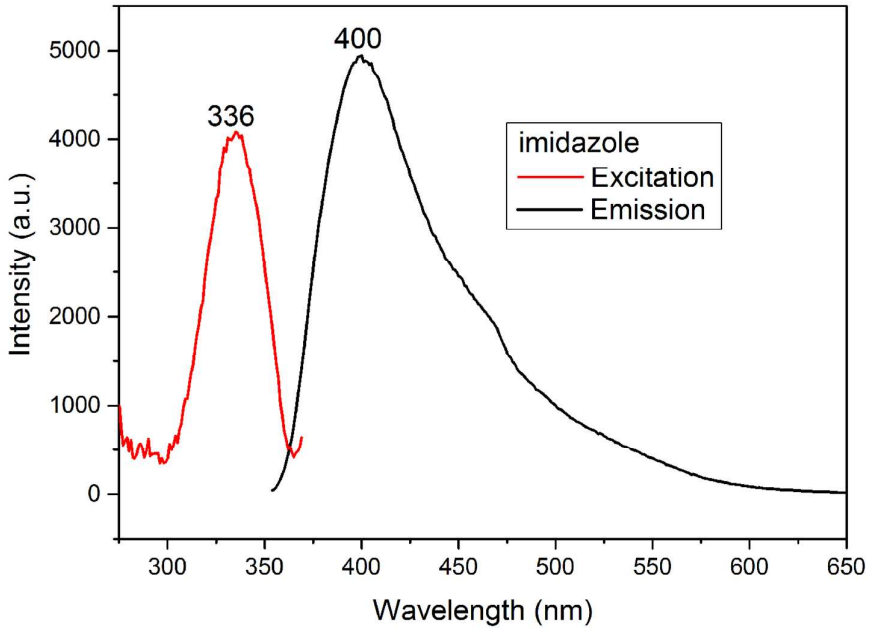

Figure S24. Excitation and emission spectra of imidazole.

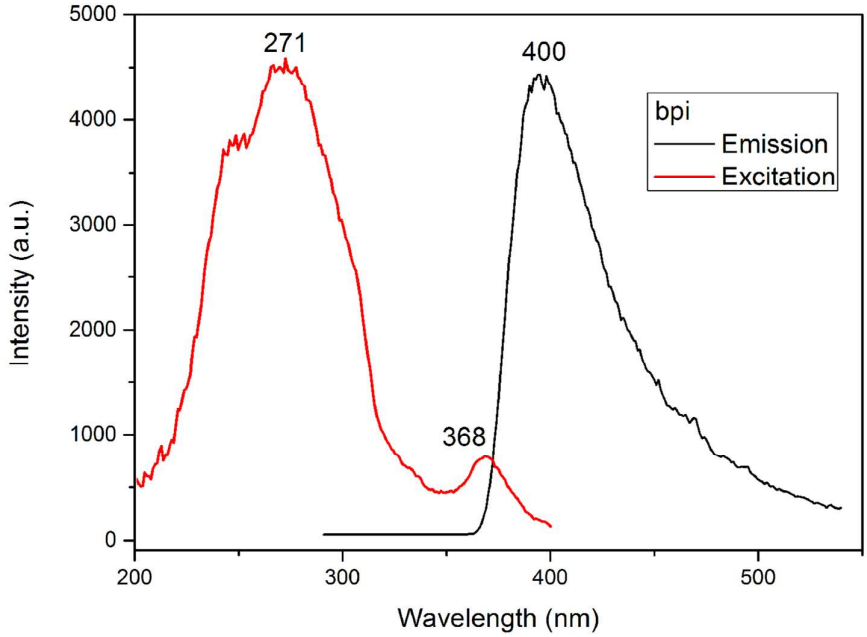

Figure S25. Excitation and emission spectra of **bpi**.

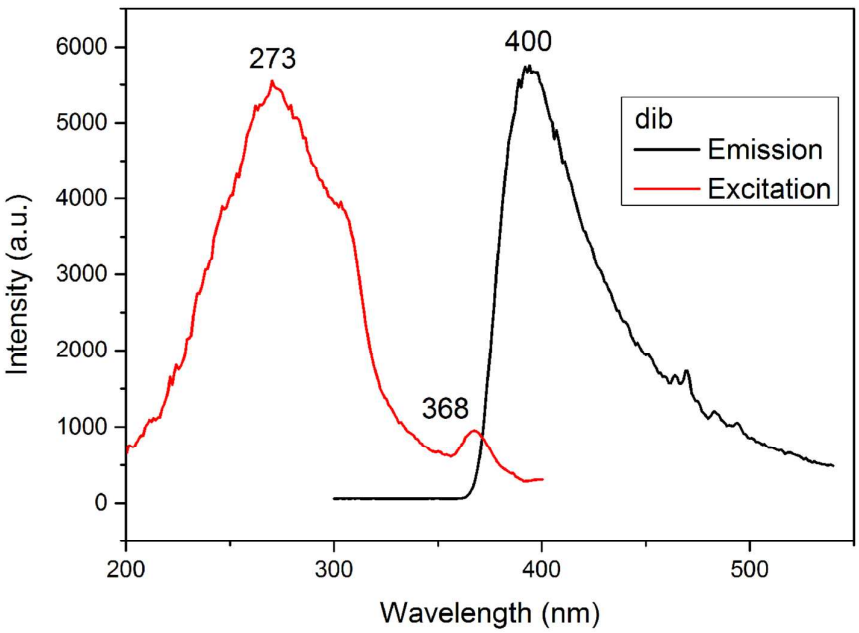

Figure S26. Excitation and emission spectra of **dib**.