Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Synthesis:

All reagents and solvents were used as received from commercial supplier without further purification.

Synthesis of $Cd(eim)_2$:

$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.534 g) and 2-ethylimidazole (0.961 g) were dissolved in 20 ml methanol, and the mixture was transferred to a 50 ml stainless steel autoclave and then heated to 120℃ for 12h. After cooling to room temperature, the products were washed with ethanol several times, and pale-yellow crystals were harvested. The phase purity was confirmed by PXRD.

Synthesis of $Zn(eim)_2$:

A solution of 2-ethylimidazole (0.384g) in 6ml methanol and another solution of $Zn(OH)_2$ (0.198g) in 40ml concentrated aqueous ammonia were mixed and stirred for three days. The products were obtained after centrifugation.

Thermal analysis:

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed under air atmosphere with a heating rate of 5℃/min using a Labsys Evo system (by SETARAM) from room temperature to 600℃. No weight occurred before 350℃, which also confirm no pores exist in the structure.

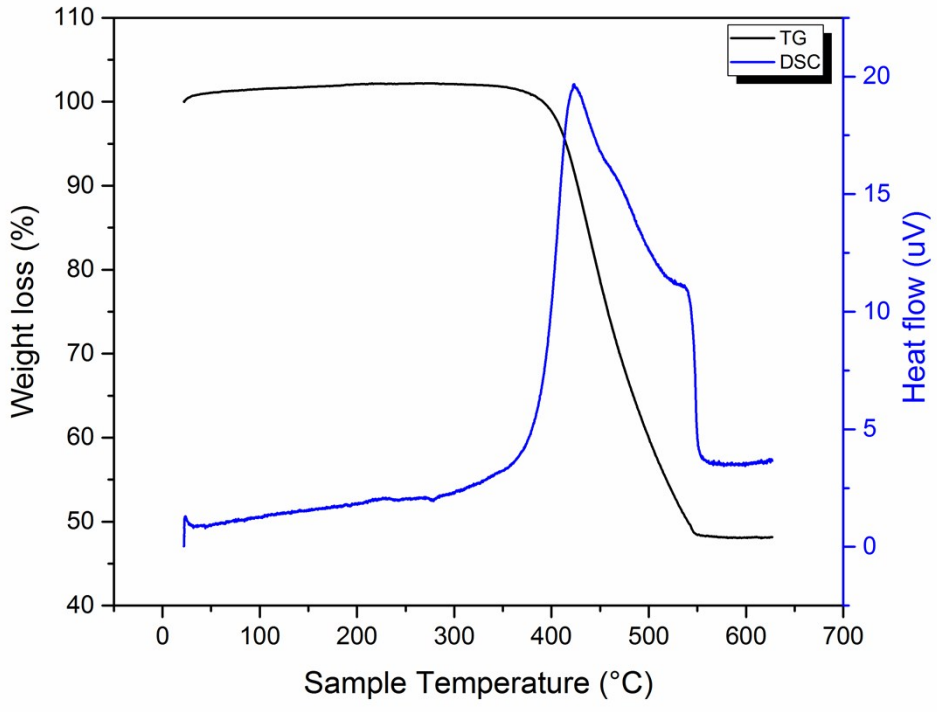

Figure S1 Thermal gravimetric analysis and differential scanning calorimetry of $Zn(eim)_2$.

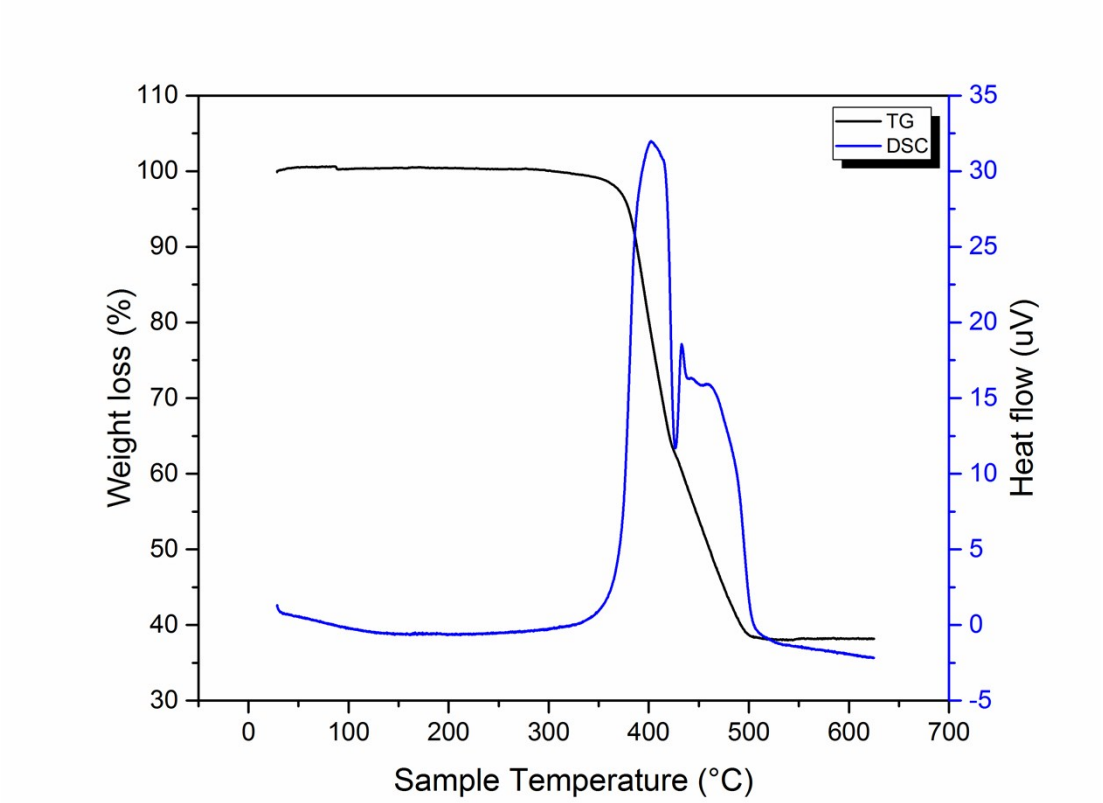

Figure S2 Thermal gravimetric analysis and differential scanning calorimetry of Cd (eim)2.

Variable temperature Powder X-ray Diffraction (VT-PXRD):

Variable temperature power x-ray diffraction (VT-PXRD) data were collected on a PANalytical diffractometer with Cu Kα radiation equipped with a TTK450 accessory and recorded in the temperature range from 123K to 473K at intervals of 25 K. The reversibility was confirmed by the cooling the sample from 423K to 123K with an interval of 100K. And Lebail fitting was used to extract the lattice parameters from the data.

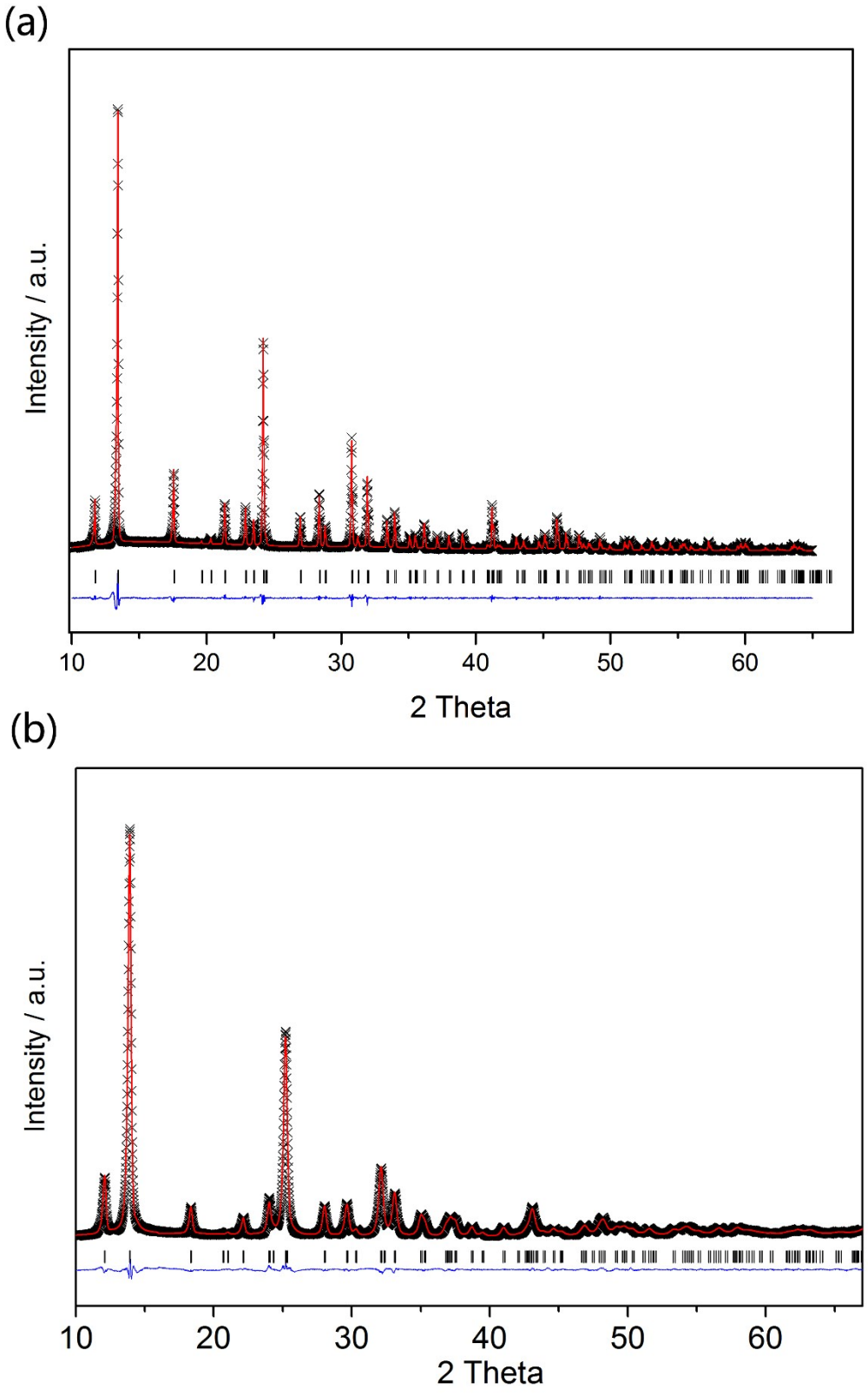

Figure S3 Lebail fitted pattern of $Cd(eim)_2$ (a) and $Zn(eim)_2$ (b) at 123K, experiment data are given as black symbols, the fitted profile as a solid red line, and the difference (data – fit) as blue line (Rp=4.52%, Rwp=5.93%, Chi2 = 6.489 for $Cd(eim)_2$, R_p=6.19%, R_{wp}= 7.39%, chi2=5.89 for $Zn(eim)_2$).

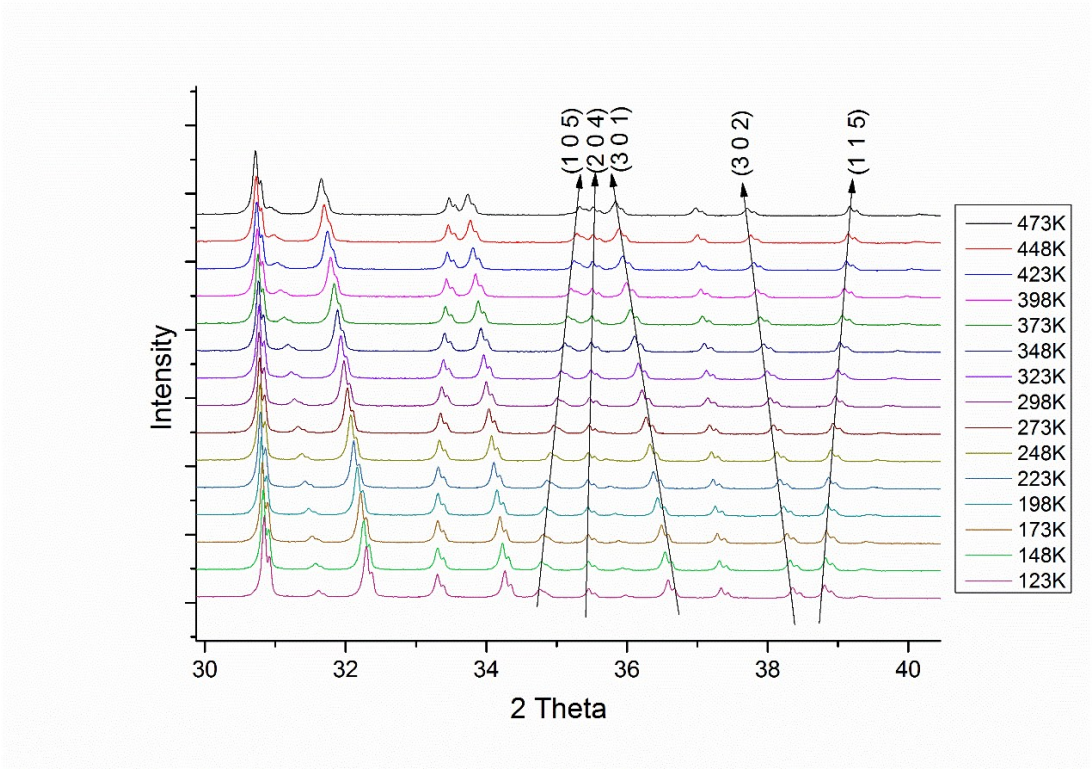

Figure S4 Part of temperature dependent powder x-ray diffraction patterns of $Cd(eim)_2$.

Table. S1 Temperature dependent lattice parameters of $Zn(eim)_2$ extracted from VTXRD using Lebail fitting.

Heating			Cooling		
Temperature/K	Lattice parameter a/Å	Lattice parameter c/Å	Temperature/K	Lattice parameter a/Å	Lattice parameter c/Å
123	8.45319(7)	12.88914(1)	423	8.52945(5)	12.81217(9)
148	8.45773(5)	12.88387(9)	323	8.50193(9)	12.84017(6)
173	8.46289(2)	12.87939(9)	223	8.47624(1)	12.86394(2)
198	8.46838(4)	12.87419(8)	123	8.45481(8)	12.88274(8)
223	8.47445(8)	12.86986(7)			
248	8.48027(8)	12.86290(5)			
273	8.48681(4)	12.85821(1)			
298	8.49326(0)	12.85138(4)			
323	8.49950(2)	12.84427(6)			
348	8.50636(8)	12.83564(7)			
373	8.51300(3)	12.82905(3)			
398	8.52000(1)	12.82140(5)			
423	8.52773(4)	12.81327(0)			
448	8.53521(2)	12.80695(7)			
473	8.54372(2)	12.79324(7)			

Table. S2 Temperature dependent lattice parameters of $Cd(eim)_2$ extracted from VTXRD using Lebail fitting.

Heating			Cooling		
Temperature/K	Lattice parameter a/Å	Lattice parameter c/Å	Temperature/K	Lattice parameter a/Å	Lattice parameter c/Å
123	8.65075(7)	13.7523(1)	423	8.82254(9)	13.5222(2)
148	8.66143(7)	13.7392(1)	323	8.76062(8)	13.6056(2)
173	8.67222(7)	13.7252(1)	223	8.70081(7)	13.6879(2)
198	8.68488(7)	13.7094(1)	123	8.65287(7)	13.7481(1)
223	8.69810(7)	13.6898(1)			
248	8.71282(5)	13.6697(1)			
273	8.72903(7)	13.6501(1)			
298	8.74459(7)	13.6283(1)			
323	8.76048(8)	13.6056(1)			
348	8.77647(8)	13.5839(2)			
373	8.79193(9)	13.5629(2)			
398	8.80715(9)	13.5423(2)			
423	8.82165(9)	13.5230(2)			
448	8.83553(9)	13.5041(2)			
473	8.8499(1)	13.4866(2)			

Variable temperature single crystal x-ray diffraction:

Variable temperature single crystal x-ray diffraction (VT-SCXRD) were collected on an Oxford Diffraction Gemini E system with Cu Kα radiation λ=1.5417 Å and the structures were solved by the direct method (SHELXS-97) and refined by full matrix least-squares (SHELXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model.

Table. S3 Temperature dependent crystallographic data of compound $Cd(eim)_2$ and atom positions of $Cd(eim)_2$ at 150K.

	150K	200K	250K	300K
Empirical formula	$C_5H_7Cd_{0.5}N_2$	$C_5H_7Cd_{0.5}N_2$	$C_5H_7Cd_{0.5}N_2$	$C_5H_7Cd_{0.5}N_2$
Formula weight	151.33	151.33	151.33	151.33
Temperature/K	150	200	250	300
Crystal system	trigonal	trigonal	trigonal	trigonal
Space group	$P3_221$	$P3_221$	$P3_221$	$P3_221$
a/Å	8.63350(10)	8.6590(2)	8.69480(10)	8.72860(10)

b/Å	8.63350(10)	8.6590(2)	8.69480(10)	8.72860(10)
c/Å	13.7402(2)	13.7050(4)	13.6675(3)	13.6174(3)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	120	120	120	120
Volume/Å^3	886.95(2)	889.91(5)	894.83(3)	898.49(3)
Z	6	6	6	6
ρ_{calc}g/cm^3	1.7	1.694	1.685	1.678
μ/mm^{-1}	14.578	14.53	14.45	14.391
F(000)	450	450	450	450
Goodness-of-fit on F^2	1.233	1.208	1.2	1.196
Final R indexes [I>=2σ (I)]	R_1 = 0.0279, wR_2 = 0.0744	R_1 = 0.0256, wR_2 = 0.0689	R_1 = 0.0340, wR_2 = 0.0851	R_1 = 0.0310, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0279, wR_2 = 0.0744	R_1 = 0.0256, wR_2 = 0.0690	R_1 = 0.0342, wR_2 = 0.0854	R_1 = 0.0312, wR_2 = 0.0784
Largest diff. peak/hole / e Å^{-3}	0.59/-1.67	0.53/-1.47	0.45/-2.15	0.37/-1.56
Flack parameter	-0.014(10)	-0.001(8)	-0.012(11)	-0.023(14)
CCDC number	1547504	1547505	1547506	1547507

Atom label	Atom type	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	Cd	0.53334(5)	0.0000	0.1667	0.0037	0.0065	0.0013	0.0000	0.0000	0.0000
N1	N	0.7748(4)	0.1742(6)	0.0823(3)	0.0060	0.0080	0.0080	0.0046	0.0034	0.0043
N2	N	0.4232(6)	0.0891(6)	0.2835(3)	0.0090	0.0120	0.0070	-0.0037	-0.0038	0.0050
C1	C	0.5110(7)	0.2060(7)	0.3552(4)	0.0070	0.0100	0.0070	0.0020	0.0010	0.005
C2	C	0.7090(8)	0.2985(9)	0.3689(4)	0.009	0.020	0.021	-0.008	-0.002	0.006
H2A	H	0.7535	0.4250	0.3792	-	-	-	-	-	-
H2B	H	0.7635	0.2862	0.3099	-	-	-	-	-	-
C3	C	0.7657(1)	0.2264(5)	0.45375(5)	0.031	0.088	0.023	-0.010	-0.013	0.041
H3A	H	0.7291	0.1031	0.4420	-	-	-	-	-	-
H3B	H	0.7104	0.2359	0.5123	-	-	-	-	-	-
H3C	H	0.8933	0.2942	0.4606	-	-	-	-	-	-
C4	C	0.8865(8)	0.1166(8)	0.0463(4)	0.013	0.010	0.014	0.006	0.004	0.010
H4	H	0.9022	0.0260	0.0725	-	-	-	-	-	-
C5	C	0.2454(8)	0.0304(8)	0.2993(4)	0.003	0.015	0.015	-0.009	-0.002	0.00
H5	H	0.1510	-0.0526	0.2614	-	-	-	-	-	-

Table. S4 Temperature dependent bond lengths and angles of $Cd(eim)_2$.

Temp	Cd-N1	Cd-N2	Cd···Cd	N2-C5	N2-C1	N1-C4	N1-C1	C4-C5	θ

eratur e(K)									
150	2.194(5)	2.191(5)	6.313	1.372(8)	1.341(8)	1.379(7)	1.344(7)	1.358(8)	106.82
200	2.195(4)	2.192(4)	6.314	1.377(7)	1.339(7)	1.381(7)	1.346(7)	1.360(8)	106.57
250	2.202(5)	2.195(5)	6.319	1.367(9)	1.338(8)	1.371(8)	1.341(8)	1.360(9)	106.25
300	2.203(5)	2.196(5)	6.319	1.373(8)	1.338(8)	1.372(8)	1.342(8)	1.356(8)	105.9

Extended X-ray Adsorption Fine Structure (EXAFS):

Zn K-edge extended X-ray absorption fine structure spectra at were recorded on beamline 1W1B at the Beijing Synchrotron Radiation Facility (BSRF) at 150K, 200K, 250K, 300K under vacuum. EXAFS data analysis was performed with the Athena and Artemis programs in IFEFFIT software. Owing to the close bond length between Zn-N1 and Zn-N2, the two paths are simplified as a same path and fitted (Fig. S5). Considering the complex structure around Zn, only the first shell was fitted.

Table. S5 Temperature dependent bond length of Zn-N extracted from EXAFS and fitted R-factor.

Temperature (K)	Zn-N	R-factor
150	2.00220	0.01077
200	2.00321	0.00913
250	2.00529	0.00719
300	2.00679	0.00757

Photoluminescence:

The variable temperature photoluminescence spectra were obtained using a FLS 980 fluorometer (Edinburgh Instruments Ltd) from 77K to 350K and the excitation wave length is 380nm.

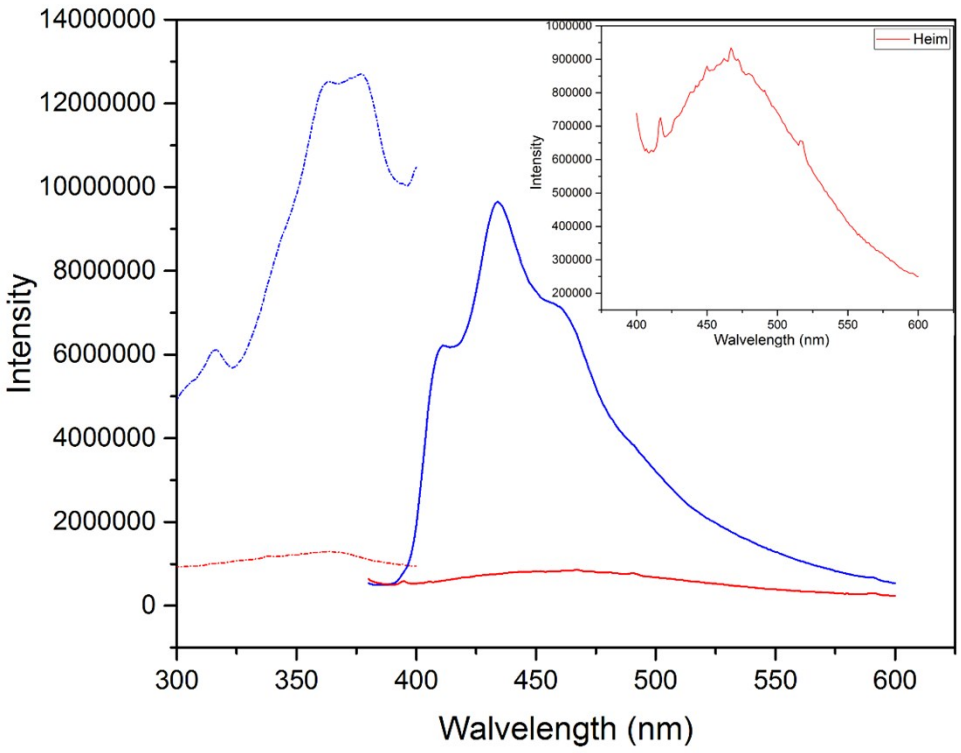

Figure S5 The excitation (…) and emission (—) spectra of $Cd(eim)_2$ (blue) and 2-ethylimidazole (red).