Supporting Information

Emission Behaviour of a Series of Bimetallic Cd(II)-Au(I) Coordination Polymers

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S1. Elemental analyses of [Cd(pyridine derivative)$_2$][Au(CN)$_2$]$_2$.

・[Cd(3-methylpyridine)$_2$][Au(CN)$_2$]$_2$

Anal. Calcd. for $C_{16}H_{14}Au_2CdN_6$ (796.67): C, 24.12; H, 1.77; N, 10.55. Found: C, 24.13; H, 1.81; N, 10.39.

・[Cd(4-ethylpyridine)$_2$][Au(CN)$_2$]$_2$

Anal, Calcd. for $C_{18}H_{18}Au_2CdN_6$ (824.72): C, 26.21; H, 2.20; N, 10.19. Found: C, 26.10; H, 2.23; N, 10.24.

10) ・[Cd(3,5-lutidine)$_2$][Au(CN)$_2$]

Anal, Calcd. for $C_{18}H_{18}Au_2CdN_6$ (824.72): C, 26.21; H, 2.20; N, 10.19. Found: C, 26.18; H, 2.29; N, 10.21.

・[Cd(3-fluoropyridine)$_2$][Au(CN)$_2$]$_2$

Anal, Calcd. for $C_{14}H_8Au_2CdN_6F_2$ (804.59): C, 20.90; H, 1.00; N, 10.45. Found: C, 20.82; H, 1.09; N, 10.52.

S2. The IR frequency of C ≡ N stretching vibration for [Cd(pyridine derivative)$_2$][Au(CN)$_2$]$_2$. The measurements were performed on KBr disks at room temperature.

・[Cd(3-methylpyridine)$_2$][Au(CN)$_2$]$_2$

IR(cm^{-1} , KBr):2170(C≡N), 1605(C=N)

・[Cd(4-ethylpyridine)$_2$][Au(CN)$_2$]$_2$

IR(cm^{-1} , KBr):2151(C≡N), 1617(C=N)

・[Cd(3,5-lutidine)$_2$][Au(CN)$_2$]$_2$

IR(cm^{-1} , KBr):2163(C≡N), 1600(C=N)

・[Cd(3-fluoropyridine)$_2$][Au(CN)$_2$]$_2$

IR(cm^{-1} , KBr):2173(C≡N), 1607(C=N)

Table S1. Crystal data for $[Cd(L)_2][Au(CN)_2]_2$

L	3-methylpyridine		4-ethylpyridine	3,5-lutidine			3-fluoropyridine
Empirical formula	$C_{16}H_{14}Au_2CdN_6$	$C_{16}H_{14}Au_2CdN_6$	$C_{36}H_{36}Au_4Cd_2N_{12}$	$C_{18}H_{18}Au_2CdN_6$			$C_{14}H_8Au_2CdF_2N_6$
Formula weight	796.67	796.67	1649.43	824.72	824.72	824.72	804.60
Temperature / K	180	90	90	298	180	90	298
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$C\,2/c$	$Pca2_1$	$Pca2_1$	$Pca2_1$	$P\,2_1/c$
a / Å	8.9854(11)	8.8666(5)	37.679(2)	15.2393(13)	15.210(3)	15.1496(19)	9.0272(18)
b / Å	15.802(2)	15.8409(9)	10.8471(6)	9.1490(8)	9.1078(14)	9.0705(11)	14.335(3)
c / Å	14.9145(19)	14.8945(9)	21.4546(13)	15.5747(13)	15.634(3)	15.6694(19)	15.885(3)
α / °	90	90	90	90	90	90	90
β / °	101.732(2)	100.9240(10)	98.9860(10)	90	90	90	94.004(3)
γ / °	90	90	90	90	90	90	90
V / Å^3	2073.4(5)	2054.1(2)	8661.0(9)	2171.5(3)	2165.8(6)	2153.2(5)	2050.7(7)
Z	4	4	8	4	4	4	4
d_{calc} / Mg m^{-3}	2.552	2.576	2.530	2.523	2.529	2.544	2.606
μ / mm^{-1}	15.142	15.285	14.505	14.463	14.501	14.586	15.325
F(000)	1432	1432	5984	1496	1496	1496	1432
ϑ range for data collection / °	1.90 to 30.99	1.90 to 31.09	2.14 to 28.28	2.23 to 29.91	2.24 to 28.28	2.25 to 28.28	1.92 to 23.67
Reflections collected	14672	15157	28300	15073	13827	13670	9224
Independent reflections	6027 [R_{int} = 0.0579]	6025 [R_{int} = 0.0284]	10716 [R_{int} = 0.0362]	5959 [R_{int} = 0.0396]	3985 [R_{int} = 0.0459]	4886 [R_{int} = 0.0375]	3076 [R_{int} = 0.0514]
GOF	0.998	0.998	1.054	0.889	0.986	0.869	1.044
R, $wR2$ [$I>2\sigma(I)$]	0.0463, 0.1161	0.0270, 0.0601	0.0528, 0.1362	0.0340, 0.0644	0.0257, 0.0511	0.0229, 0.0456	0.0468, 0.1105
R, $wR2$ (all data)	0.0636, 0.1280	0.0415, 0.0647	0.0574, 0.1407	0.0521, 0.0709	0.0318, 0.0531	0.0280, 0.0473	0.0780, 0.1223
Flack parameter [1)]	-	-	-	0.024(7)	0.033(7)	0.031(5)	-
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	1.569, -3.077	1.461, -2.185	8.72, -4.458	0.859, -1.084	1.033, -1.485	1.703, -1.389	1.656, -1.085

$R = \Sigma||F_0| - |F_c|| / \Sigma|F_o|$, $wR2 = \{\Sigma w(|F_0| - |F_c|)^2 / \Sigma w(F_o)^2\}^{1/2}$

Reference 1) H. D. Flack, *Acta Crystallogra., Sect. A*, 1983, A**39**, 876.

Table S2. Selected bond lengths for $[Cd(L)_2][Au(CN)_2]_2$

L = 3-methylpyridine			
180 K		90 K	
Cd1-N1	2.353(6)	Cd1-N1	2.325(4)
Cd1-N2	2.330(5)	Cd1-N2	2.334(4)
Cd1-N3	2.343(6)	Cd1-N3	2.328(4)
Cd1-N4	2.329(5)	Cd1-N4	2.353(4)
Cd1-N5	2.376(5)	Cd1-N5	2.357(3)
Cd1-N6	2.367(6)	Cd1-N6	2.361(4)
Au1-C3[1]	1.994(6)	Au1-C1[1]	1.976(4)
Au1-C4	1.989(6)	Au1-C4	1.987(4)
Au2-C1[2]	1.985(6)	Au2-C2[2]	1.980(4)
Au2-C2[3]	1.978(6)	Au2-C3[3]	1.988(4)
Au1-Au2	3.1479(6)	Au1-Au2	3.1271(3)
Symmetry codes		Symmetry codes	
1: x,-y+1/2,z+1/2		1: x,-y+1/2,z+1/2	
2: -x+1,-y+1,-z+1		2: -x+1,y-1/2,-z+1/2	
3: -x+1,y-1/2,-z+1/2		3: -x+1,-y+1,-z+1	

L = 4-ethylpyridine			
90 K			
Au1-C1	1.986(8)	Cd1-N10	2.308(7)
Au1-C19	1.981(8)	Cd1-N8	2.369(7)
Au2-C35[1]	1.985(8)	Cd1-N9	2.353(7)
Au2-C36	1.985(8)	Cd1-N11	2.366(7)
Au3-C2[2]	1.999(8)	Cd1-N12	2.350(7)
Au3-C4	1.993(8)	Cd2-N1	2.405(7)
Au4-C3	1.994(9)	Cd2-N2	2.335(8)
Au4-C34[3]	1.992(8)	Cd2-N3	2.333(7)
Au1-Au2[4]	3.0941(5)	Cd2-N4	2.351(8)
Au2-Au3[5]	3.2467(5)	Cd2-N5	2.291(7)
Au3-Au4[6]	3.1219(4)	Cd2-N6	2.304(7)
Cd1-N7	2.331(7)		
Symmetry codes			
1: x, y+1, z			
2: x, −y+1, z−1/2			
3: x−1/2, y+1/2, z			
4: −x+1/2, y−1/2, −z+1/2			
5: −x+1/2, y+1/2, −z+1/2			
6: −x, y, −z+1/2.			

L = 3,5-lutidine					
298 K		180 K		90 K	
Cd1-N1	2.407(8)	Cd1-N1	2.394(7)	Cd1-N1	2.380(6)
Cd1-N2	2.376(7)	Cd1-N2	2.411(7)	Cd1-N2	2.386(5)
Cd1-N3	2.379(8)	Cd1-N3	2.383(7)	Cd1-N3	2.380(5)
Cd1-N4	2.409(7)	Cd1-N4	2.369(6)	Cd1-N4	2.386(6)
Cd1-N5	2.327(6)	Cd1-N5	2.326(6)	Cd1-N5	2.329(5)
Cd1-N6	2.337(8)	Cd1-N6	2.338(6)	Cd1-N6	2.323(5)
Au1-C1	1.992(9)	Au1-C1	1.980(8)	Au1-C1	1.998(7)
Au1-C4[1]	2.002(9)	Au1-C4[1]	1.995(8)	Au1-C4[1]	2.007(7)
Au2-C2[2]	1.974(9)	Au2-C2[2]	2.010(8)	Au2-C2[2]	1.985(6)
Au2-C3	1.990(9)	Au2-C3	2.008(9)	Au2-C3	2.005(7)
Au1-Au2[3]	3.1440(6)	Au1-Au2[3]	3.1419(6)	Au1-Au2[3]	3.1345(5)
Symmetry codes		Symmetry codes		Symmetry codes	
1: -x+5/2,y,z+1/2		1: -x+1/2,y,z-1/2		1: -x+5/2,y,z+1/2	
2: -x+3/2,y,z-1/2		2: -x+3/2,y,z+1/2		2: -x+3/2,y,z-1/2	
3: -x+2,-y+1,z+1/2		3: -x+1,-y+1,z-1/2		3: -x+2,-y+2,z+1/2	

L = 3-fluoropyridine	
298 K	
Cd1-N1	2.304(13)
Cd1-N2	2.328(13)
Cd1-N3	2.319(14)
Cd1-N4	2.351(13)
Cd1-N5	2.406(12)
Cd1-N6	2.383(11)
Au1-C1	2.004(16)
Au1-C4[1]	1.991(18)
Au2-C2[2]	1.999(16)
Au2-C3	1.949(17)
Au1-Au2[3]	3.1874(11)
Symmetry codes	
1: x,-y+3/2,z+1/2	
2: x,-y+5/2,z-1/2	
3: -x+1,y-1/2,-z+3/2	

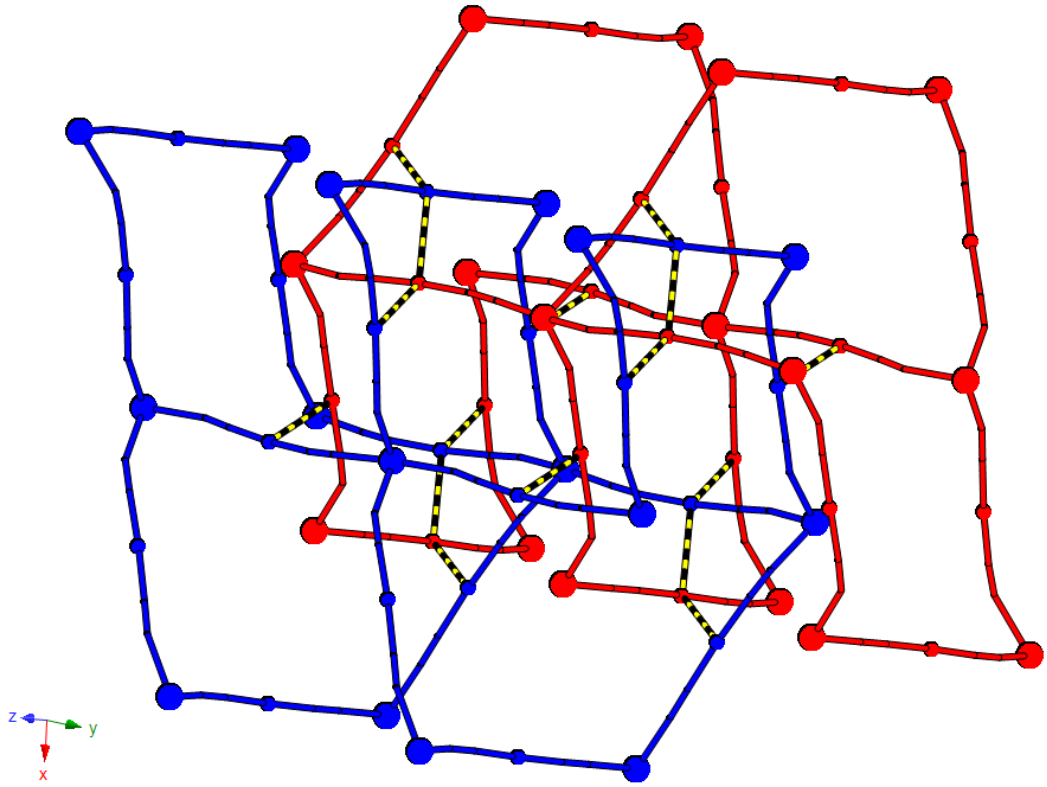

Figure S1. Doubly interpenetrated $Cd[Au(CN)_2]_2$ frameworks (red and blue) of $[Cd(4\text{-ethylpyridine})_2][Au(CN)_2]_2$

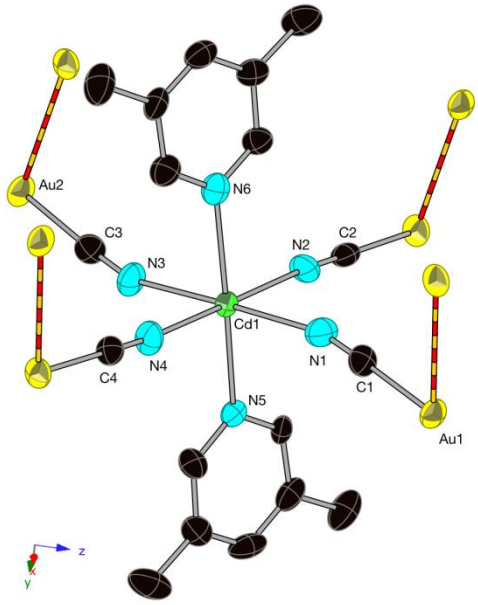

Figure S2. Local structure around Cd(II) ion of $[Cd(3,5\text{-lutidine})_2][Au(CN)_2]_2$.
Displacement ellipsoids are drawn 50 % probability level.
H atoms are omitted for clarity.

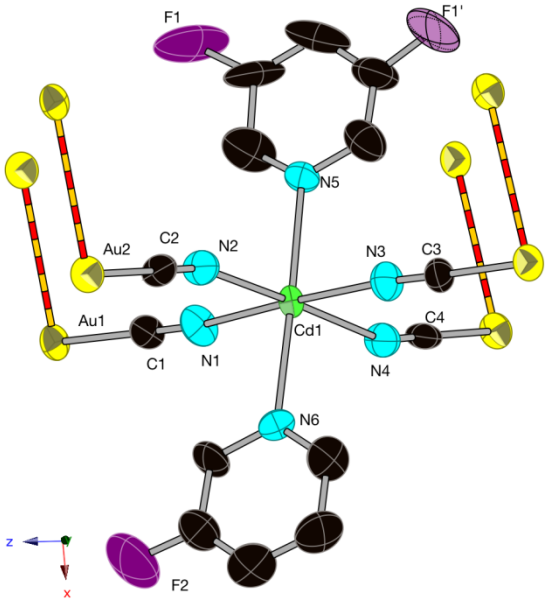

Figure S3. Local structure around Cd(II) ion of $[Cd(3\text{-fluoropyridine})_2][Au(CN)_2]_2$.
Displacement ellipsoids are drawn 30 % probability level.
H atoms are omitted for clarity.

S4. Comparison of the power diffraction patterns of [Cd(4-ethylpyridine)$_2$][Au(CN)$_2$]$_2$ between the power and crystalline samples

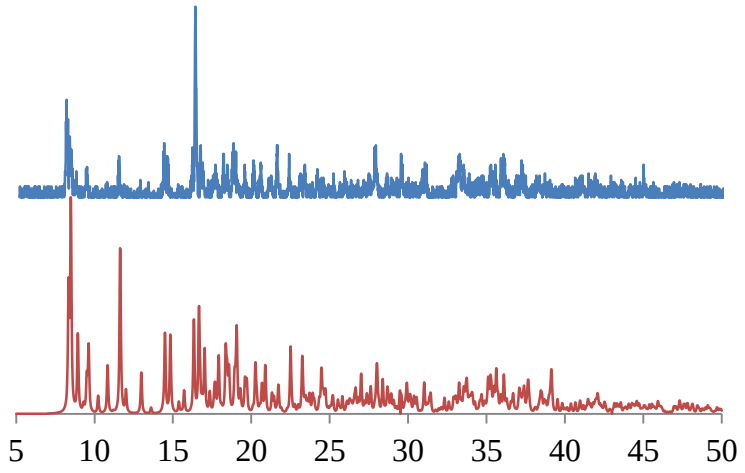

Figure S4.The X-ray diffraction patterns of the powder sample of [Cd(4-ethylpyridine)$_2$][Au(CN)$_2$]$_2$: (upper) the prepared sample and (lower) the simulation from the single crystal X-ray analysis.

S5. The temperature dependence of the decay rates of the emission from

[Cd(4-ethylpyridine)$_2$][Au(CN)$_2$]$_2$.

Table S3: The results of two components in the decay of mission at various temperatures

	Relaxation time (μs)		Fractions	
Temperature[K]	fast	slow	fast	slow
183	0.932	2.442	0.0381	1.95E-02
193	1.081	2.752	0.0425	1.05E-02
203	1.137	7.438	0.0498	1.31E-03
213	0.896	17.222	0.0504	7.67E-04
223	0.676	35.875	0.049	6.96E-04
233	0.492	20.283	0.0445	6.03E-04
243	0.351	42.672	0.0389	8.51E-04
253	0.262	17.104	0.0309	5.70E-04
263	0.178	35.754	0.0197	4.56E-04
273	0.152	16.249	0.0164	6.38E-04
283	0.132	48.914	0.0111	8.63E-04
293	0.118	26.395	0.0068	6.75E-04

The rate of the fast decay component ($1/\tau_i$: i = 1) is plotted against temperature (K) as below:

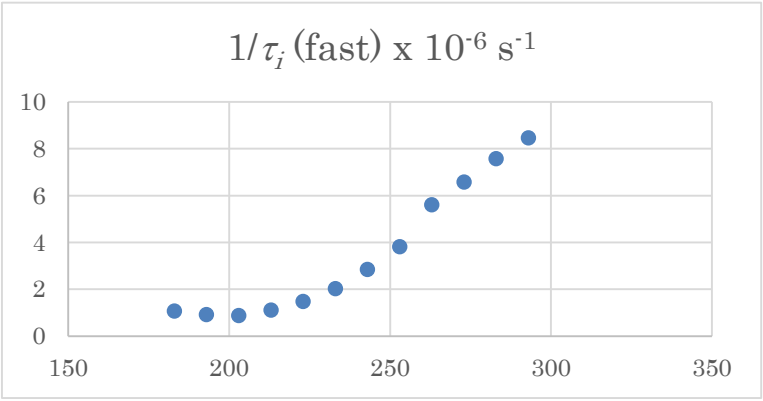

Figure S5. The plot of the rate of emission decay against temperature in case of $[Cd(4\text{-ethylpyridine})_2][Au(CN)_2]_2$.

The rate of the spontaneous emission ($1/\tau_r(se)$) is obtained to be $1.0x10^6$ s^{-1} by extrapolating the plot to T = 0 K on the assumption that it was independent of temperature. By assuming the relation that $1/\tau_i = 1/\tau_r(se) + 1/\tau_r(nr)$, the natural logarithm of $1/\tau_r(nr) = 1/\tau_i - 1/\tau_r(se)$ is plotted against 1/T as below:

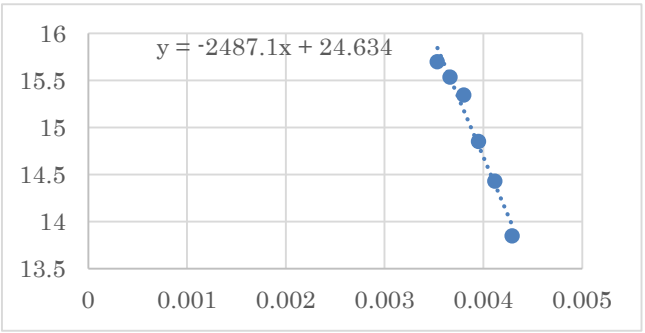

Figure S6. The plot of the rate of non-radiative decay against temperature in case of $[Cd(4\text{-ethylpyridine})_2][Au(CN)_2]_2$.

From the slope of the activation energy for $1/\tau_r(nr)$ was obtained to be 20.7 kJ mol^{-1} (or 1700 cm^{-1}). As for the slow component in the decay of emission, no such analysis was performed since the rate value of k_2 was so scattered because of the error involved.

S6. The excitation spectra of $[Cd(pyridine\ derivative)_2][Au(CN)_2]_2$

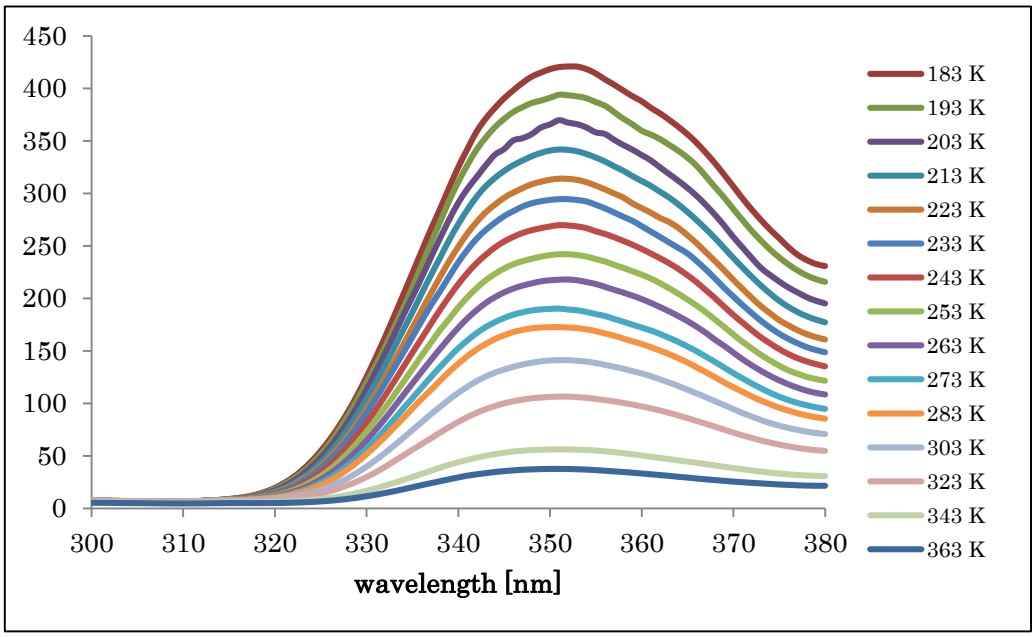

Figure S7. Excitation Spectra of $[Cd(4\text{-ethylpyridine})_2][Au(CN)_2]_2$ (λ_{em}=460 nm)

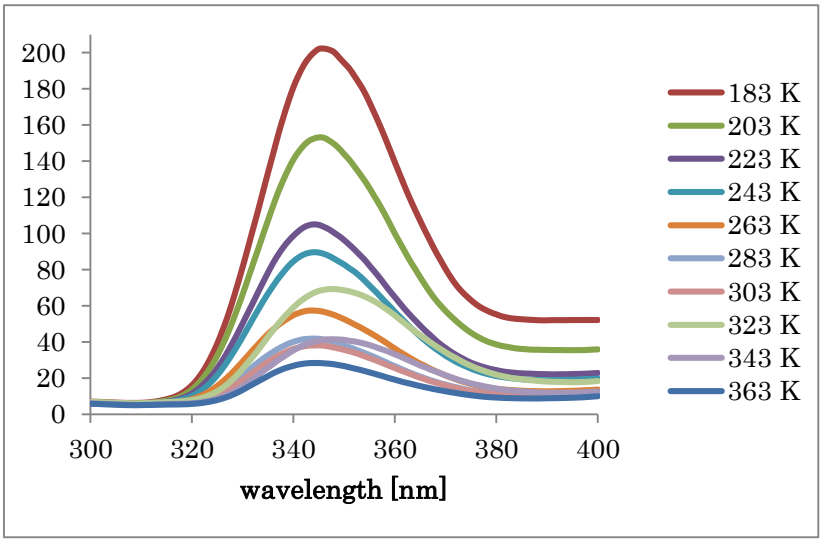

Figure S8.Excitation Spectra of $[Cd(3,5\text{-lutidine})_2][Au(CN)_2]_2$ (λ_{em}=460 nm)

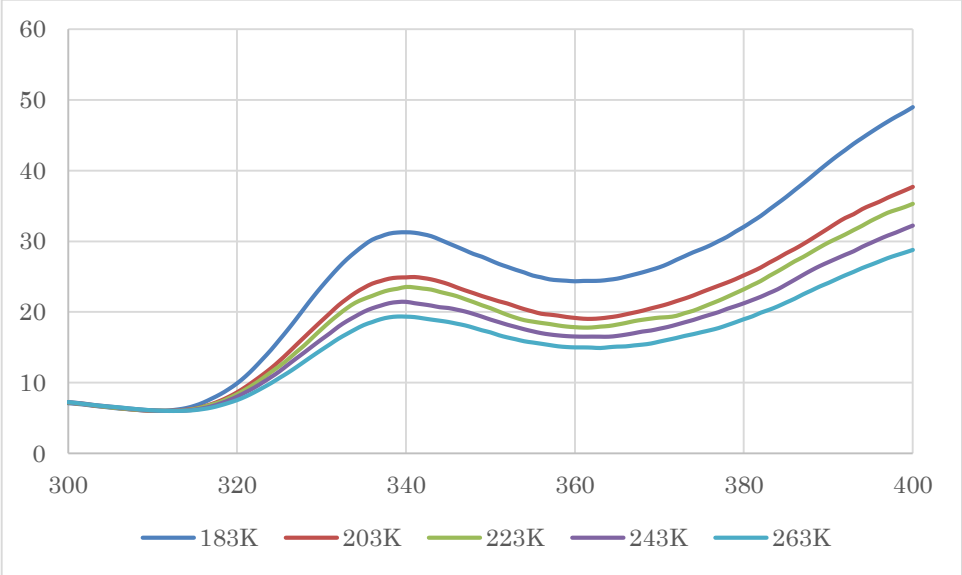

Figure S9. Excitation Spectra of $[Cd(3\text{-fluoropyridine})_2][Au(CN)_2]_2$($\lambda_{em}$ =440 nm)