Supporting Information

for

Structure and photoluminescence property of two-dimentional coordination polymer complexes involving $Cu^{I}_{6}X_{6}$ (X = Cl, Br, I) hexagon prism cluster supported by a tripodal tripyridine ligand with 1,3,5-triethylbenzen spacer

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Experimental

General. Reagents and solvents used in this study except the ligand and complexes were commercial products of the highest available purity and were further purified by the standard methods, if necessary.[1] Ligand L and $[Cu^{I}(CH_3CN)_4](PF_6)$ have been synthesized according to the reported methods.[2,3] FT-IR spectra were recorded with a Shimadzu FTIR-8200PC. UV-vis spectra were obtained on a Hewlett Packard 8453 photo diode array spectrophotometer. Reflection spectra of the solid sample (rubbed on a filter paper) were taken on a Shimadzu UV2550 with the integrating-sphere attachment ISR-2200. Fluorescence spectra of the solid sample (rubbed on a filter paper) were taken on a JASCO FP-6300. Mass spectra were obtained on a JEOL JMS-700T Tandem MS-station mass spectrometer. Elemental analysis was carried out on a Perkin-Elmer 240C or a Fisons instruments EA1108 Elemental Analyzer.

X-ray Structure Determination. The single crystal was mounted on a glass-fiber. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector using graphite-monochromated Mo*K*α radiation (λ = 0.71069 Å) to 2θ max of 55°. All the crystallographic calculations were performed by using Crystal Structure software package of the Molecular Structure Corporation [Crystal Structure: Crystal Structure Analysis Package version 3.7.0, Molecular Structure Corp. and Rigaku Corp. (2000-2005)]. The crystal structures were solved by the direct methods and refined by the full-matrix least squares using SHELX97 (for $[Cu^{I}_6Cl_6L_2]_n$ and $[Cu^{I}_6Br_6L_2]_n$) and SIR92 (for $[Cu^{I}_6I_6L_2]_n$ and $[Cu^{I}L]PF_6$. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. Atomic coordinates, thermal parameters, and intramolecular bond distances and angles are deposited in the supplementary materials (CIF file format).

Synthesis

$([Cu^{I}_6Cl_6L_2])_n$. A solution of L (326.7 mg, 0.684 mmol) in acetone (2.0 mL) was

added slowly to a suspension of $Cu^{I}Cl$ (203.7 mg, 2.05 mmol) in acetone (8.0 mL) under anaerobic conditions (in a glove box DBO-1KP (Miwa Co. Ltd.); $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). White powder was immediately precipitated. After the mixture was stirred for additional 27 h, the precipitate was collected by filtration to give white powder (486.0 mg, 92%). Single crystals suitable for the X-ray analysis were obtained by recrystallization from a mixed solvent system consisted of $CHCl_3/CH_3CN$ ($v : v = 1 : 1$)/Et_2O. IR (KBr): 772, 2868, 2903, 2926, and 2961 cm^{-1}; Anal. calcd for $[Cu^{I}_6Cl_6L_2]$, $C_{33}H_{39}Cl_3Cu_3N_3$: C; 51.16, H; 5.07, N; 5.42. found for C; 50.96, H; 4.99, N; 5.43.; UV-vis (solid sample): λ_{max} = 215, 265, and 345 nm.

$([Cu^{I}_6Br_6L_2])_n$. In the glove box ($[O_2] < 1$ ppm, $[H_2O] < 1$ ppm), single crystals suitable for the X-ray analysis were obtained by liquid-phase diffusion between a CH_3CN solution (12.0 mL) of $Cu^{I}Br$ (30.5 mg, 21.3 x 10^{-5} mol) and a CH_2Cl_2 solution (3.0 mL) of L (33.5 mg, 7.0 x 10^{-5} mol) in a glass tube (ϕ = 0.6 cm) (25.4 mg, 40%). IR (KBr): 770, 2868, 2903, 2926, and 2963 cm^{-1}; Anal. calcd for $[Cu^{I}_6Br_6L_2]$, $C_{33}H_{39}Br_3Cu_3N_3$: C; 43.67, H; 4.23, N; 4.63. found for C; 43.65, H; 4.33, N; 4.63; UV-vis (solid sample): λ_{max} = 215, 265, 300, and 345 nm.

$([Cu^{I}_6I_6L_2])_n$. Single crystals suitable for the X-ray analysis were obtained by liquid-phase diffusion between a CH_3CN solution (80.0 mL) of $Cu^{I}I$ (596.0 mg, 3.13 x 10^{-3} mol) and a CH_2Cl_2 solution (20.0 mL) of L (494.9 mg, 1.04 x 10^{-3} mol) in a glass tube (ϕ = 0.6 cm) (658.0 mg, 65%). IR (KBr): 752. 768, 2866, 2903, and 2966 cm^{-1}; Anal. calcd for $[Cu^{I}_6I_6L_2]$, $C_{33}H_{39}Cu_3I_3N_3$: C; 37.79, H; 3.63, N; 4.03. found for C; 37.79, H; 3.75, N; 4.01; UV-vis (solid sample): λ_{max} = 220, 263, and 305nm.

$[Cu^{I}(L)](PF_6)$. To a suspension of $[Cu_I(CH_3CN)_4](PF_6)$ (70.3 mg, 0.189 mmol) in acetone (0.5 mL) was added slowly a solution of L (90.0 mg, 0.189 mmol) in acetone (3.0 mL) under anaerobic conditions (in a glove box, $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The suspension was turned to a yellow solution. After stirring for 25 h, insoluble materials were removed by filtration. The filtrate was concentrated by evaporation under reduced pressure.

Addition of Et_2O (15 mL) to the residue gave pale yellow precipitate. Careful decantation of the precipitate gave pale yellow powder (107.5 mg, 83%). Single crystals suitable for the X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. IR (KBr): 841 (PF_6^{-1}) cm^{-1}; HRMS (FAB, pos): m/z = 540.2435 calcd for ($[Cu^I+L]^+$, $C_{33}H_{39}CuN_3$ 540.2440); Anal. calcd for $[Cu^I(L)](PF_6)$, $C_{33}H_{39}CuF_6N_3P$: C; 57.76, H; 5.73, N; 6.12. found for C; 57.89, H; 5.75, N; 6.10; UV-vis: (solid sample) λ_{max} = 220, 267, and 310 nm, (1.0 x 10^{-4} M, CH_2Cl_2) λ_{max} = 303 nm, (1.0 x 10^{-4} M, acetonitrile) λ_{max} = 256, 262, and 268 nm.

References

1 W. L. F. Armarego, D. D. Perrin, In *Purification of Laborator Chemicals*, 4th ed. Butterworth-Heinemann; Oxford, 1996; pp176 and 215.

2 H. Ohi, Y. Tachi, S. Itoh, *Inorg. Chem.* 2004, **43**, 4561.

3 G. J. Kubas, *Inorg. Synth.* 1979, **19**, 90.

Figure S1

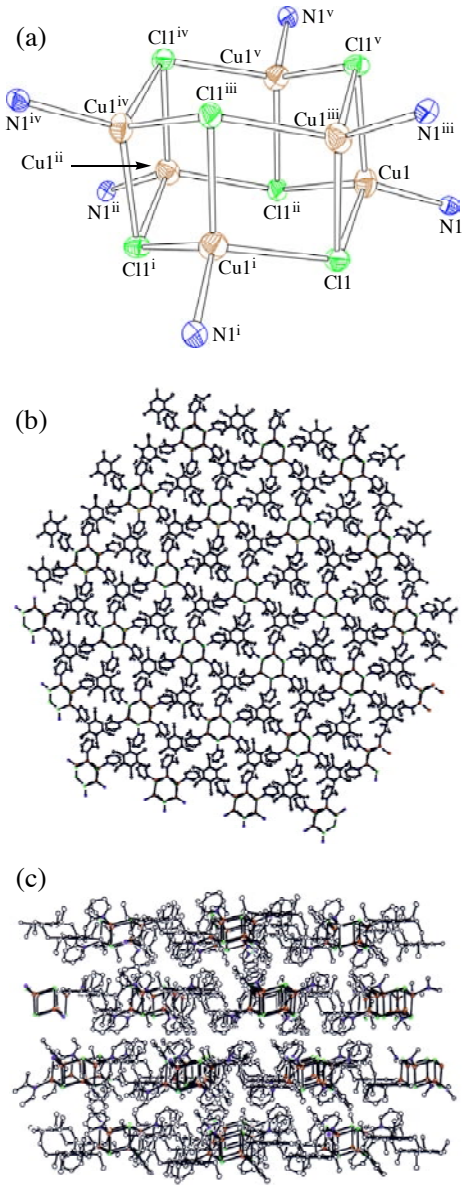

Figure S1. ORTEP drawings of $([Cu^{I}_{6}Cl_{6}L_{2}])_{n}$ showing 50% probability thermal ellipsoid; (a) the $[Cu^{I}_{6}Cl_{6}L_{2}]$ core structure, (b) a top view, and (c) a side view. Hydrogen atoms are omitted for clarity. Symmetry codes: i = (2–x+y, 2–x, z), ii = (2–y, x–y, z), iii = (2/3+y, 4/3–x+y, 1/3–z), iv = (8/3–x, 4/3–y, 1/3–z), v = (2/3+x–y, –2/3+x, 1/3–x).

Table S1. Summary of X-ray Crystallographic Data

Compound	$([\mathbf{Cu^{I}_{6}Cl_{6}L_{2}}])_{n}$
formula	$C_{33}H_{39}N_{3}Cu_{3}Cl_{3}$
formula weight	774.69
crystal system	trigonal
space group	*R*-3 (#148)
a, Å	15.029(4)
b, Å	15.029(4)
c, Å	23.744(8)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	4644.7(24)
Z	6
F(000)	2376.00
D_{calcd}, g/cm^{-3}	1.662
T, K	163
crystal size, mm	0.25 x 0.25 x 0.08
μ (MoKα), cm^{-1}	23.298
$2\theta_{max}$, deg	55.0
no. of reflns measd	14463
no. of reflns obsd	1948 ([$I > 2.00\sigma(I)$])
no. of variables	141
R[a], Rw[b]	0.0254, 0.0272
goodness of fit indicator	1.023

[a] $R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$ [b] $R_W = [\, \Sigma \, w \, (|F_o| - |F_c|)^2 \, / \, \Sigma \, w \, F_o^2 \,]^{1/2}$

Table S2. Selected Bond Lengths (Å) and Angles (deg) of $([Cu^{I}_{6}Cl_{6}L_{2}])_{n}$[a]

Selected bond length

Cu1-Cl1	2.4265(5)	Cu1-Cl1^{ii}	2.3660(8)
Cu1-Cl1^{v}	2.3943(5)	Cu1-N1	2.0155(18)
Cu1-Cu1^{iii}	2.9281(3)	Cu1-Cu1^{i}	4.0969(3)
Cu1-Cu1^{iv}	5.0357(3)		

Selected bond angles

Cl1-Cu1-Cl1^{ii}	107.66(2)	Cl1-Cu1-Cl1^{v}	103.441(18)
Cl1-Cu1-N1	107.16(5)	Cl1^{ii}-Cu1-Cl1^{v}	105.31(2)
Cl1^{ii}-Cu1-N1	115.58(6)	Cl1^{v}-Cu1-N1	116.74(5)
Cu1-Cl1-Cu1^{iii}	74.799(15)	Cu1-Cl1-Cu1^{i}	117.48(2)
Cu1^{iii}-Cl1-Cu1^{i}	75.918(16)		

[a]Estimated standard deviations are given in parentheses.

Figure S2

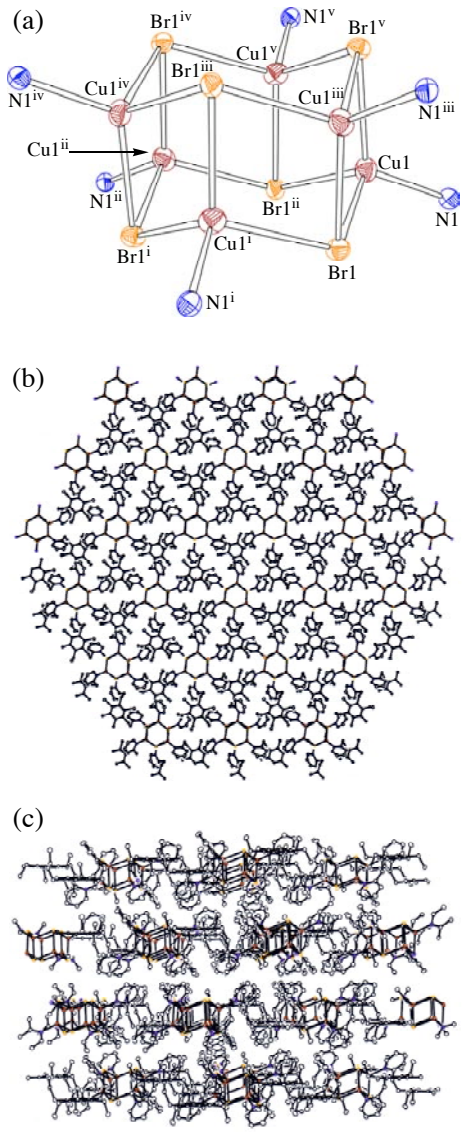

Figure S2. ORTEP drawings of $([Cu^{I}_{6}Br_{6}L_{2}])_{n}$ showing 50% probability thermal ellipsoid; (a) the $[Cu^{I}_{6}Br_{6}L_{2}]$ core structure, (b) a top view, and (c) a side view. Hydrogen atoms are omitted for clarity. Symmetry codes: i = (2–x+y, 2–x, z), ii = (2–y, x–y, z), iii = (2/3+y, 4/3–x+y, 1/3–z), iv = (8/3–x, 4/3–y, 1/3–z), v = (2/3+x–y, –2/3+x, 1/3–x).

Table S3. Summary of X-ray Crystallographic Data

Compound	$([\mathbf{Cu^{I}_{6}\ Br_{6}L_{2}}])_{n}$
formula	$C_{33}H_{39}N_3Cu_3Br_3$
formula weight	908.04
crystal system	trigonal
space group	*R*-3 (#148)
a, Å	15.1677(9)
b, Å	15.1677(9)
c, Å	24.4621(18)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	4873.8(5)
Z	6
F(000)	2700.00
D_{calcd}, g/cm^{-3}	1.856
T, K	163
crystal size, mm	0.28 x 0.20 x 0.10
μ (MoKα), cm^{-1}	56.746
$2\theta_{max}$, deg	55.0
no. of reflns measd	15918
no. of reflns obsd	2121 ([$I > 2.00\sigma(I)$])
no. of variables	141
R[a], Rw[b]	0.0237, 0.0264
goodness of fit indicator	1.018

[a] $R = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$ [b] $R_W = [\ \Sigma\ w\ (|F_o| - |F_c|)^2 / \Sigma\ w\ F_o^2]^{1/2}$

Table S4. Selected Bond Lengths (Å) and Angles (deg) of $([Cu^{I}_{6}Br_{6}L_{2}])_{n}$[a]

Selected bond length

Cu1-Br1	2.5582(4)	Cu1- Br1^{ii}	2.5101(6)
Cu1- Br1^{v}	2.4713(3)	Cu1-N1	2.034(2)
Cu1-Cu1^{iii}	2.9263(4)	Cu1-Cu1^{i}	4.2370(4)
Cu1-Cu1^{iv}	5.1493(5)		

Selected bond angles

Br1-Cu1-Br1^{ii}	104.564(16)	Br1-Cu1-Br1^{v}	107.442(14)
Br1-Cu1-N1	106.47(6)	Br1^{ii}-Cu1-Br1^{v}	108.97(2)
Br1^{ii}-Cu1-N1	110.96(7)	Br1^{v}-Cu1-N1	117.55(6)
Cu1-Br1-Cu1^{iii}	71.136(12)	Cu1-Br1-Cu1^{i}	13.433(18)
Cu1^{iii}-Br1-Cu1^{i}	71.948(13)		

[a]Estimated standard deviations are given in parentheses.

Figure S3

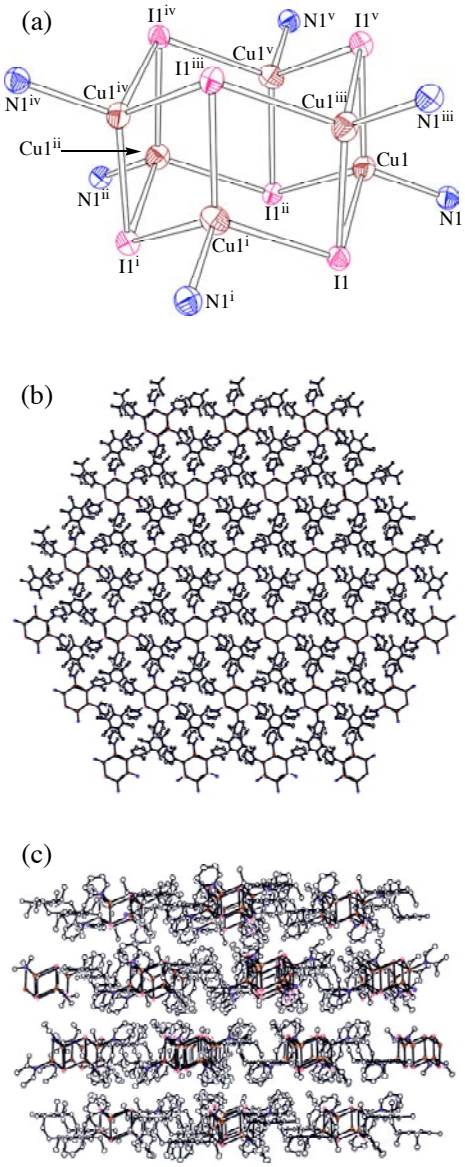

Figure S3. ORTEP drawings of $([Cu^{I}_{6}I_{6}L_{2}])_{n}$ showing 50% probability thermal ellipsoid; (a) the $[Cu^{I}_{6}I_{6}L_{2}]$ core structure, (b) a top view, and (c) a side view. Hydrogen atoms are omitted for clarity. Symmetry codes: i = (2–x+y, 2–x, z), ii = (2–y, x–y, z), iii = (y+2/3, 4/3–x+y, 1/3–z), iv = (8/3–x, 4/3–y, 1/3–z), v = (2/3+x–y, –2/3+x, 1/3–x).

Table S5. Summary of X-ray Crystallographic Data

Compound	$([Cu^{I}_{6}\ I_6L_2])_n$
formula	$C_{33}H_{39}N_3Cu_3I_3$
formula weight	1049.04
crystal system	trigonal
space group	*R*-3 (#148)
a, Å	15.3547(17)
b, Å	15.3547(17)
c, Å	25.539(5)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	5214.5(12)
Z	6
F(000)	3024.00
D_{calcd}, g/cm^{-3}	2.004
T, K	163
crystal size, mm	0.09 x 0.07 x 0.15
μ (MoKα), cm^{-1}	45.109
$2\theta_{max}$, deg	54.9
no. of reflns measd	16836
no. of reflns obsd	2142 ([$I > 2.00\sigma(I)$])
no. of variables	141
R^a, Rw^b	0.0203, 0.0230
goodness of fit indicator	1.032

$^aR = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$ $^bR_W = [\ \Sigma\ w\ (|F_o| - |F_c|)^2 / \Sigma\ w\ F_o^2]^{1/2}$

Table S6. Selected Bond Lengths (Å) and Angles (deg) of $([Cu^{I}_{6}I_{6}L_{2}])_{n}$[a]

Selected bond length

Cu1-I1	2.7248(4)	Cu1-I1^{ii}	2.6628(5)
Cu1-I1^{v}	2.5991(5)	Cu1-N1	2.063(2)
Cu1-Cu1^{iii}	2.9645(5)	Cu1-Cu1^{i}	4.3834(4)
Cu1-Cu1^{iv}	5.2918(6)		

Selected bond angles

I1-Cu1-I1^{ii}	102.451(16)	I1-Cu1-I1^{v}	110.755(15)
I1-Cu1-N1	106.68(7)	I1^{ii}-Cu1-I1^{v}	112.75(2)
I1^{ii}-Cu1-N1	106.61(8)	I1^{v}-Cu1-N1	116.49(7)
Cu1-I1-Cu1^{iii}	67.627(14)	Cu1-I1-Cu1^{i}	108.895(16)
Cu1^{iii}-I1-Cu1^{i}	68.570(15)		

[a]Estimated standard deviations are given in parentheses.

Figure S4

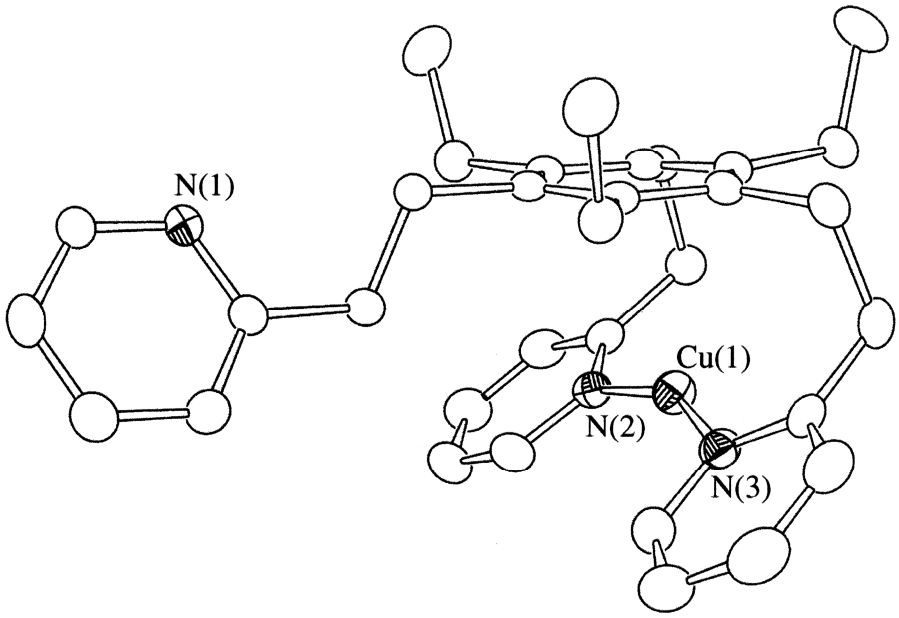

Figure S4. An ORTEP drawing of $[Cu^{I}L](PF_6)$ showing 50% probability thermal ellipsoid. Hydrogen atoms and counter anion are omitted for clarity.

Table S7. Summary of X-ray Crystallographic Data

Compound	**$[Cu^{I}L](PF_6)$**
formula	$C_{33}H_{39}N_3CuPF_6$
formula weight	686.20
crystal system	triclinic
space group	*P*-1 (#2)
a, Å	10.027(4)
b, Å	10.254(3)
c, Å	16.081(6)
α, deg	82.509(14)
β, deg	77.487(19)
γ, deg	82.478(17)
V, Å^3	1591.3(10)
Z	2
F(000)	712.00
D_{calcd}, g/cm^{-3}	1.432
T, K	160
crystal size, mm	0.22 x 0.30 x 0.15
μ (MoKα), cm^{-1}	7.995
$2\theta_{max}$, deg	55.0
no. of reflns measd	15670
no. of reflns obsd	5961 ([$I > 2.00\sigma(I)$])
no. of variables	436
R[a], Rw[b]	0.0400, 0.0593
goodness of fit indicator	1.002

[a] $R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$ [b] $R_W = [\, \Sigma \, w \, (|F_o| - |F_c|)^2 \, / \, \Sigma \, w \, F_o^2 \,]^{1/2}$

Table S8. Selected Bond Lengths (Å) and Angles (deg) of $[Cu^{I}L](PF_6)$[a]

Selected bond length	
Cu1-N2	1.9182(16)
Cu1-N3	1.9176(16)
Selected bond angles	
N1-Cu1-N2	154.11(7)

[a]Estimated standard deviations are given in parentheses.

Figure S5

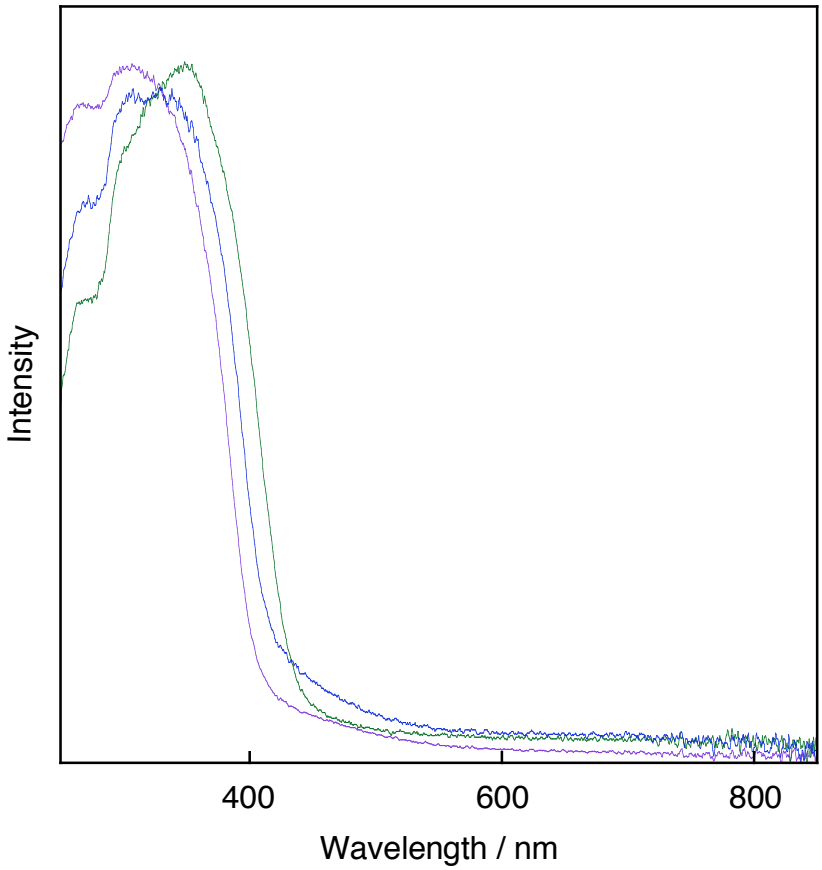

Figure S5. Reflection spectra of 2D polymer complexes $([Cu^{I}_{6}X_{6}L_{2}])_{n}$ (green; X = Cl, blue; X = Br, purple; X = I). Maximum intensities normalized.

Figure S6

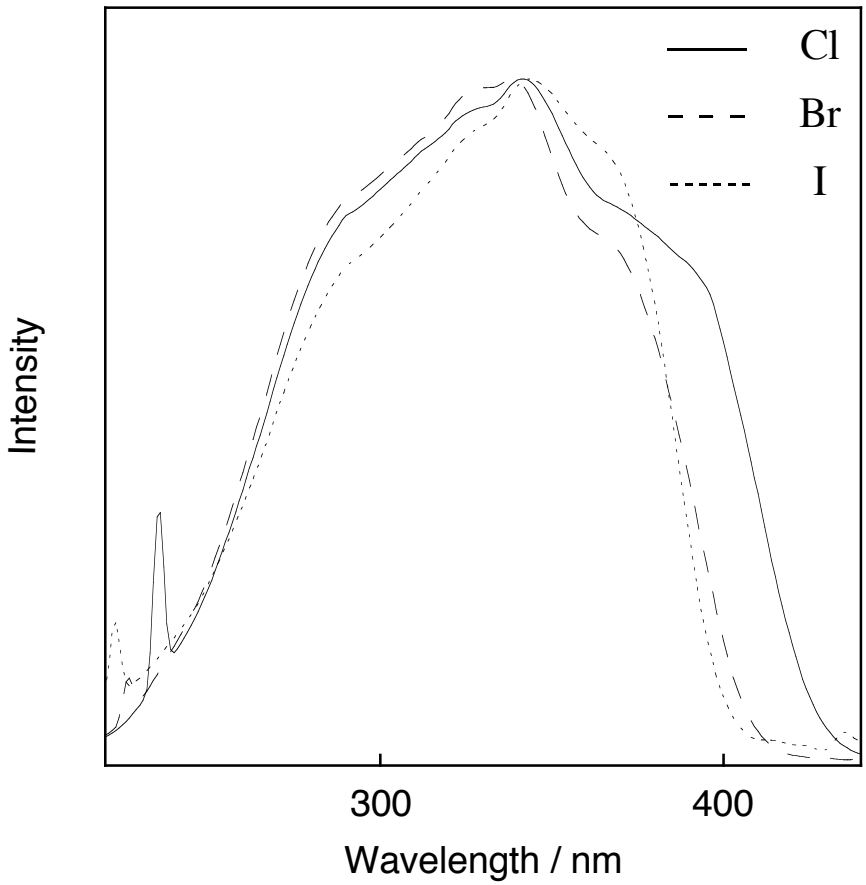

Figure S6. Excitation spectra of the solid sample of $[Cu^{I}_{6}X_{6}L_{2}]_{n}$.: excitation spectra monitoring at 476nm (X = Cl, λ^{ex}_{max} = 341 nm), 455 nm (X = Br, λ^{ex}_{max} = 339 nm), and 448 nm (X = I, λ^{ex}_{max} = 343 nm). Maximum intensities normalized.