Supplementary Material (ESI) for Chemical Communications

Flexibility of cubane-like Cu_4I_4 framework: Temperature dependence of molecular structure and luminescence thermochromism of $[Cu_4I_4(PPh_3)_4]$ in two polymorphic crystalline states.

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Electronic Supplementary Information

X-ray Crystallography:

S ingle crystal X-ray diffraction measurements for **1a** and **1b** above 100 K were performed on a Rigaku Rapid image plate diffractometer using Mo$K\alpha$ (λ = 0.7107 Å) radiation. A sample crystal was mounted on a glass capillary kept under a cold nitrogen gas stream from a cryostat. A large cylindrical image plate diffractometer at the SPring-8 BL02B1 beamline was used with a helium gas-flow type cryostat in the lower temperature region, The X-ray radiation from a bending magnet, monochromatized by Si(111) double crystals (λ = 0.5886 Å). Collected intensity data were merged after empirical absorption corrections. The initial structures were determined by Pattersion method[1]. All non-hydrogen atoms were refined applying anisotropic displacement parameters. All hydrogen atoms were located by calculation inferred from attached carbon atoms and were constrained with a riding model during the refinements. The summaries of the crystallographic data fo**r** 1a an**d** 1b at various temperatures are listed in **Table S1** and **S2**, respectively. Selected bond distances and bond angles at room temperature and 20 K are listed in **Table S3**. Packing diagrams for 1a and 1b are given in **Figure S2**. The solvent accessible void space calculations were performed for checking a possibility of including solvent of crystallizations by using *PLATON*[2], in which the grid points (0.2 Å grid step) isolated more than 1.2 Å from the nearest van der Waals surface were searched. The maximum volumes of the void spaces of **1a** and **1b** are 36 Å^3 and 39 Å^3, respectively.

1. G. Sheldrick, *Acta Cryst.*, 2008, A**64**, 112-122.
2. A.L.Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2010.

Table S1 Crystallographic data for $[Cu_4I_4(PPh_3)_4]$ monoclinic form(**1a**).

T / K	400	350	294	203
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	13.6362 (8)	13.5817 (3)	13.5413 (10)	13.4801 (3)
b / Å	27.2233 (15)	27.1007 (6)	26.949 (2)	26.6785 (5)
c / Å	19.5261 (11)	19.4851 (5)	19.4847 (14)	19.4749 (3)
β / °	98.9500 (10)	98.9690 (10)	99.0220 (10)	99.1380 (10)
V /Å^3	7160.3 (7)	7084.3 (3)	7022.5 (9)	6914.8 (2)
Z	4	4	4	4
D_x /g cm^{-3}	1.680	1.698	1.713	1.739
λ / Å	0.7107	0.7107	0.7107	0.7107
$\mu(\lambda)$ /mm^{-1}	1.70	1.72	1.73	1.76
2θ range / deg	3.0—30.0	3.0—30.0	3.0—27.5	3.0—30.0
crystal size / mm	0.20×0.18×0.10	0.20×0.18×0.10	0.22×0.14×0.12	0.34×0.20×0.12
refln. measured	70075	83348	65738	120896
refln. indep. (R_{int})	20567 (0.084)	20606 (0.068)	15986 (0.092)	19992 (0.059)
no. of param.	757	757	757	757
ρ_{min} , ρ_{max} / eÅ^{-3}	−1.82, 1.75	−1.84, 1.19	−0.52, 0.61	−1.08, 1.13
GOF on F^2	1.05	1.08	1.02	1.09
R^a, Rw^b	0.075, 0.280	0.043, 0.142	0.054, 0.092	0.035, 0.066

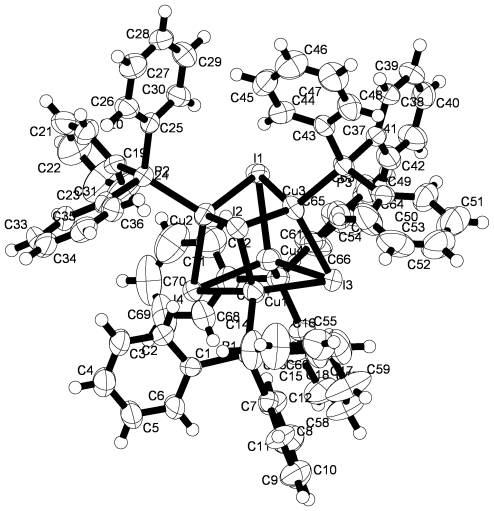
153	103	77	45	20
$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
13.4525 (3)	13.4230 (3)	13.4031 (3)	13.3915 (3)	13.3862 (2)
26.5559 (5)	26.4422 (5)	26.3883 (5)	26.3236 (5)	26.2858 (5)
19.4660 (3)	19.4442 (3)	19.3872 (14)	19.3799 (14)	19.3801 (14)
99.2370 (10)	99.3060 (10)	99.305 (7)	99.366 (7)	99.410 (7)
6863.9 (2)	6810.6 (2)	6766.7 (5)	6740.6 (5)	6727.5 (5)
4	4	4	4	4
1.752	1.766	1.778	1.784	1.788
0.7107	0.7107	0.58860	0.58860	0.58860
1.77	1.79	1.80	1.81	1.81
3.1—30.0	3.1—30.0	1.3—24.5	1.3—24.5	1.3—24.5
0.34×0.20×0.12	0.34×0.20×0.12	0.10×0.05×0.03	0.10×0.05×0.03	0.10×0.05×0.03
119932	110779	110090	109408	109078
19852 (0.053)	19710 (0.050)	19775 (0.040)	19695 (0.044)	19657 (0.047)
757	757	757	757	757
−0.91, 1.08	−1.04, 1.31	−0.91, 0.94	−1.01, 0.78	−0.98, 0.90
1.07	1.08	0.75	0.81	0.88
0.030, 0.056	0.028, 0.052	0.018, 0.032	0.018, 0.034	0.018, 0.038

Table S2 Crystallographic data for $[Cu_4I_4(PPh_3)_4]$ monoclinic form(**1b**).

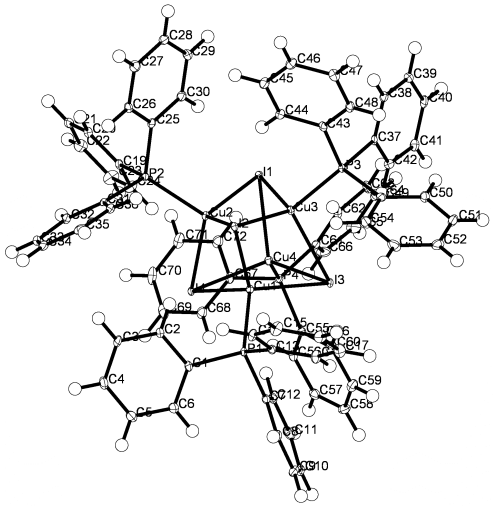
T / K	300	203	153	105
Space group	*I*-43*d*	*I*-43*d*	*I*-43*d*	*I*-43*d*
a / Å	30.1826 (5)	29.9834 (5)	29.9058 (5)	29.8333 (5)
V /Å^3	27496.0 (8)	26955.2 (8)	26746.5 (8)	26552.4 (8)
Z	16	16	16	16
D_x /g cm^{-3}	1.750	1.785	1.799	1.812
λ / Å	0.7107	0.7107	0.7107	0.7107
$\mu(\lambda)$ /mm^{-1}	1.77	1.81	1.82	1.83
2θ range / deg	3.0—30.0	3.0—30.0	3.1—30.0	3.1—30.0
crystal size / mm	0.24×0.18×0.16	0.24×0.22×0.22	0.24×0.22×0.22	0.24×0.22×0.22
refln. measured	112088	22781	47686	60655
refln. indep. (R_{int})	6669 (0.070)	6264 (0.043)	6483 (0.043)	6444 (0.039)
no. of param.	253	253	253	253
ρ_{min} , ρ_{max} / eÅ^{-3}	−1.23, 0.76	−0.91, 0.90	−1.26, 1.00	−1.16, 0.54
GOF on F^2	1.03	1.14	1.16	1.17
R[a], Rw[b]	0.060, 0.168	0.038, 0.146	0.035, 0.179	0.030, 0.154
Flack param.	0.00 (4)	0.02 (4)	0.08 (4)	0.08 (4)

77	45	20
I-43*d*	*I*-43*d*	*I*-43*d*
29.8024 (5)	29.7569 (5)	29.7325 (5)
26470.0 (8)	26348.9 (8)	26284.2 (8)
16	16	16
1.818	1.826	1.830
0.58860	0.58860	0.58860
1.84	1.85	1.85
1.4—24.5	1.4—24.5	1.4—24.5
0.11×0.10×0.06	0.11×0.10×0.06	0.11×0.10×0.06
171294	170976	170782
6455 (0.039)	6439 (0.040)	6421 (0.067)
253	253	253
−0.24, 0.26	−0.28, 0.22	−0.44, 0.26
1.08	1.10	1.04
0.012, 0.030	0.011, 0.029	0.013, 0.033
0.014 (9)	0.017 (8)	0.015 (9)

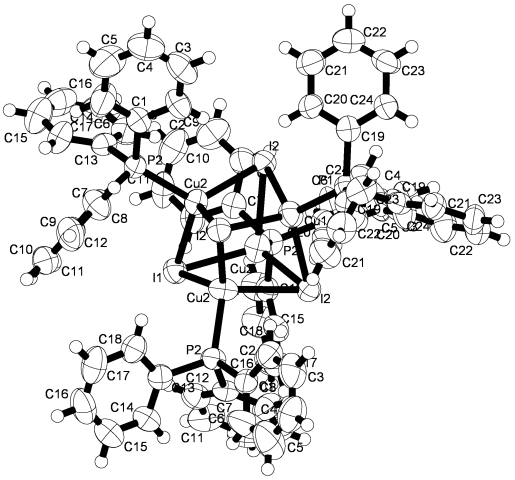
[a]$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $[F_o^2 > 2\sigma(F_o^2)]$. [b]$R_w = [\Sigma w(F_o^2 - F_c^2) / \Sigma w(F_c^2)]^{1/2}$, (all data).



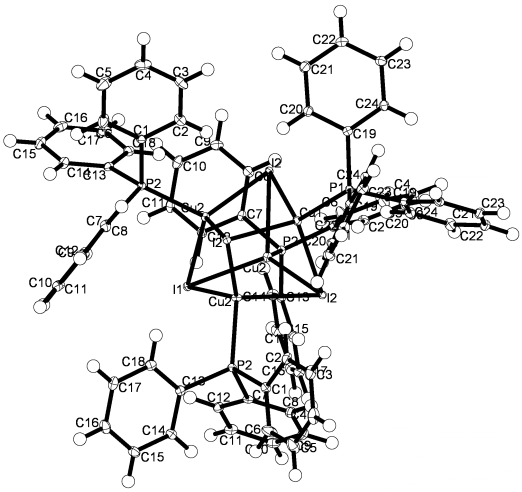
(**1a**) at 294K



(**1a**) at 20 K

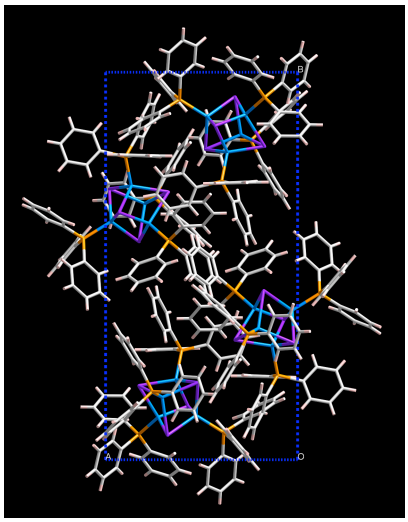


(**1b**) at 300 K

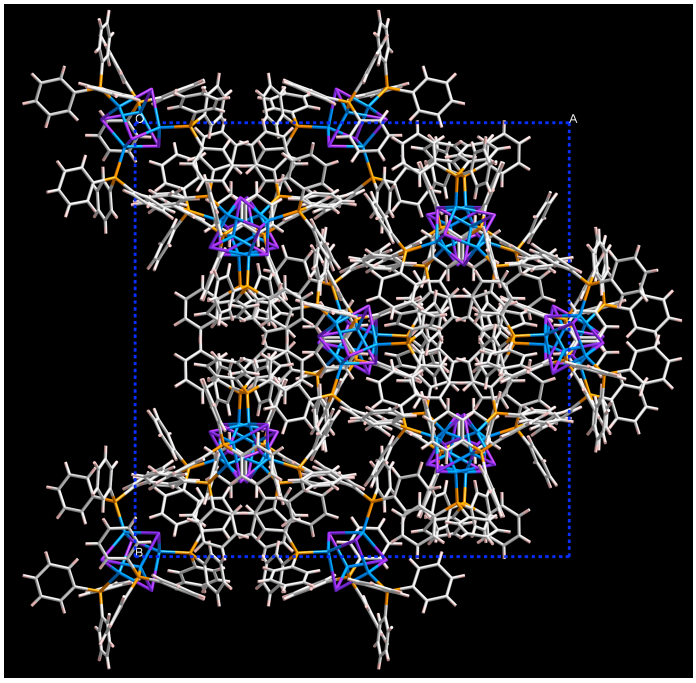


(**1b**) at 20 K

Figure S1. ORTEP drawings of molecular structures of **1a** and **1b** with 50 % probability ellipsoids.



1a (monoclinic form) projected along the *c*-axis.



1b (cubic form) projected along the *a*-axis.

Figure S2. Packing diagrams of **1a** (294 K) and **1b** (300 K).

Table S3. Selected inter-atomic distances (Å) and angles (°) in **1a** (294K, 20K) and **1b**(300K, 20K).

1a	294 K	20 K	**1b**	300 K	20 K
I4—Cu1	2.6620 (8)	2.6383 (3)	I2—Cu2	2.6249 (13)	2.6198 (2)
I4—Cu4	2.6909 (9)	2.6815 (3)	I2—Cu1	2.7155 (9)	2.70205 (17)
I4—Cu2	2.7078 (8)	2.6945 (2)	I2—Cu2^{i}	2.7987 (14)	2.7771 (2)
I3—Cu1	2.6547 (9)	2.6558 (2)			
I3—Cu3	2.6973 (9)	2.6782 (2)			
I3—Cu4	2.7195 (9)	2.6906 (3)			
I2—Cu3	2.6704 (9)	2.6704 (3)			
I2—Cu2	2.6892 (9)	2.6769 (3)			
I2—Cu1	2.7353 (9)	2.6978 (3)			
I1—Cu3	2.6700 (9)	2.6601 (3)			
I1—Cu2	2.7057 (8)	2.6787 (3)			
I1—Cu4	2.7141 (9)	2.7037 (2)			
Cu1—P1	2.2531 (16)	2.2536 (5)	Cu1—P1	2.279 (4)	2.2686 (7)
Cu2—P2	2.2579 (16)	2.2530 (5)	Cu2—P2	2.255 (2)	2.2530 (4)
Cu3—P3	2.2518 (17)	2.2506 (5)			
Cu4—P4	2.2608 (18)	2.2625 (5)			
Cu1—Cu4	2.8676 (11)	2.7783 (3)	Cu1—Cu2	3.1775 (19)	3.0849 (4)
Cu1—Cu3	2.8971 (10)	2.7896 (3)	Cu2—Cu2^{i}	2.9478 (19)	2.8041 (3)
Cu1—Cu2	2.9277 (10)	2.7917 (3)			
Cu4—Cu3	3.1084 (11)	2.9716 (4)			
Cu4—Cu2	3.1658 (10)	3.0587 (3)			
Cu2—Cu3	2.8400 (10)	2.7299 (4)			
I3—Cu1—I4	115.07 (3)	115.830 (10)	I2—Cu1—I2^{i}	104.77 (4)	105.916 (8)
I3—Cu1—I2	107.81 (3)	111.658 (9)	I2—Cu2—I1	112.89 (5)	115.009 (8)
I4—Cu1—I2	108.83 (3)	108.764 (9)	I2—Cu2—I2^{ii}	104.93 (5)	106.081 (8)
I1—Cu3—I2	114.93 (3)	115.958 (10)	I1—Cu2—I2^{ii}	107.58 (4)	109.979 (7)
I1—Cu3—I3	105.47 (3)	108.275 (9)			
I2—Cu3—I3	108.47 (3)	108.915 (8)			
I4—Cu4—I1	103.21 (3)	106.647 (9)			
I4—Cu4—I3	112.01 (3)	112.805 (9)			
I1—Cu4—I3	103.65 (3)	103.498 (8)			
I2—Cu2—I1	113.13 (3)	115.102 (10)			
I2—Cu2—I4	108.85 (3)	110.963 (9)			
I1—Cu2—I4	102.98 (3)	104.532 (9)			

Symmetry codes for **1b**: (i) $z, x-1, y+1$; (ii) $y+1, z-1, x$.

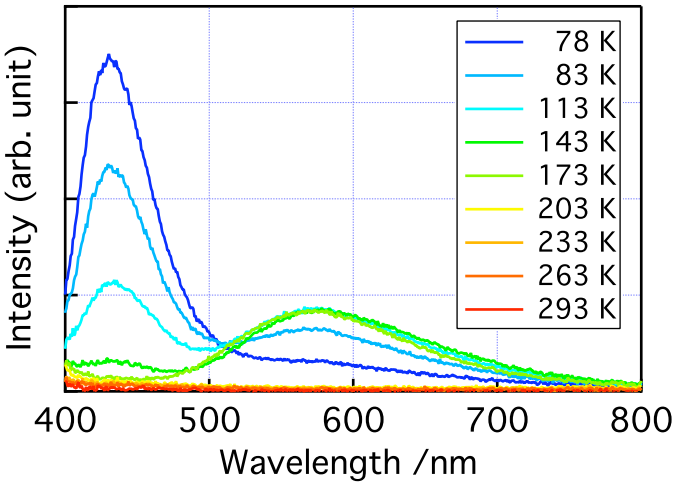


Figure S4. Photoemission spectra of $[Cu_4I_4(PPh_3)_4]$ in toluene solution (5.5×10^{-4} M).