Supplementary information

Structure and Luminescence Color Change of Iridium(III) Bis-Terpyridine Complex Crystal Triggered by Water Sorption/Desorption

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(i) Thermogravimetry (TG) results

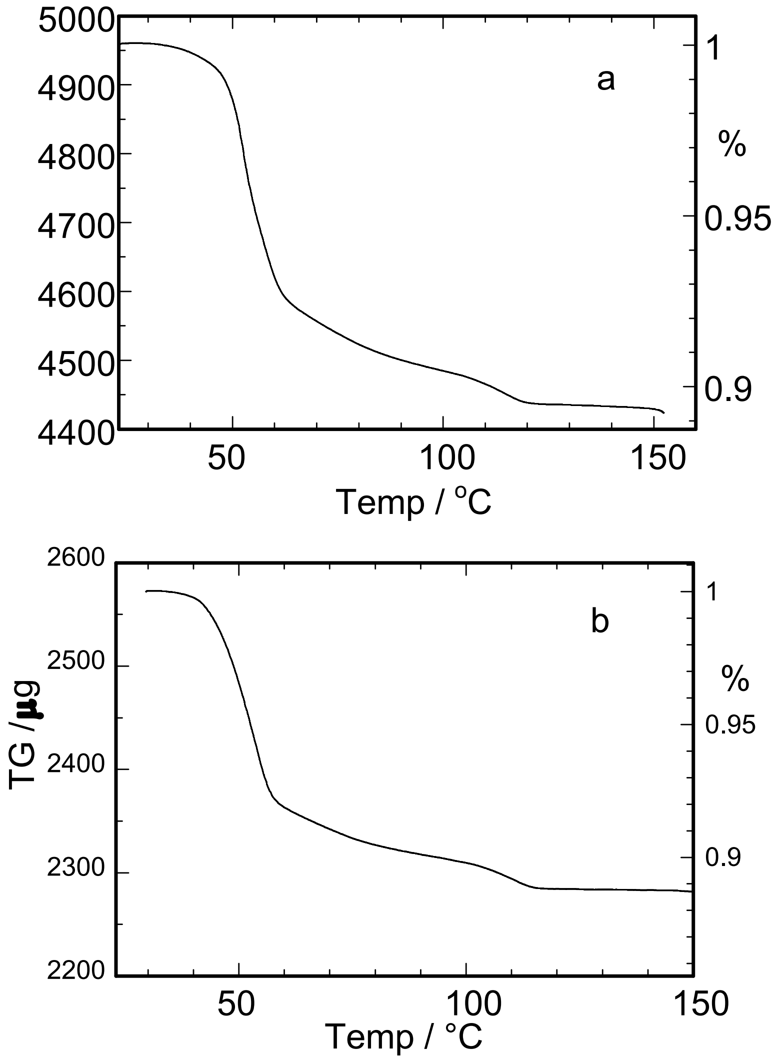


Fig. S1. TG curves for 4.96 mg (a) and 2.57 mg (b) $[Ir(tpy)_2]Br_3$ salts experienced the heating at 150°C and the cooling at ambient temperature under the humid condition. The numbers of crystal waters are determined as 6.0184 and 6.4087, respectively.

(ii) A DSC result for $[Ir(tpy)_2]Br_3 \cdot 7H_2O$ (M7)

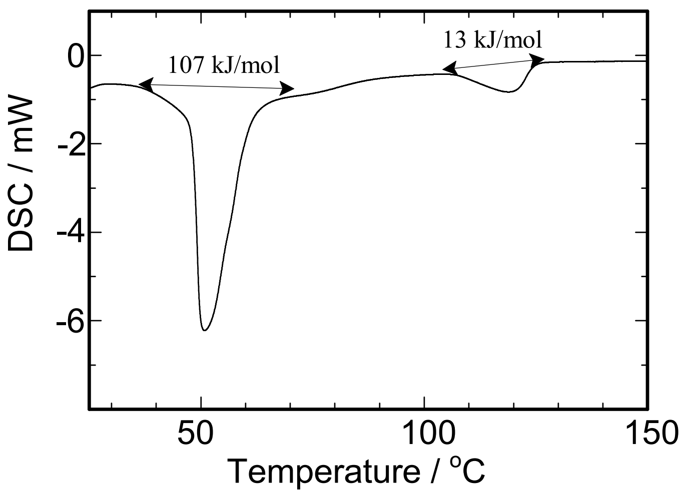
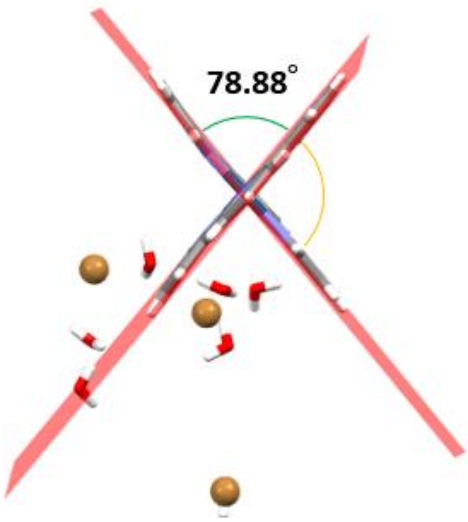


Fig. S2. A DSC curve for **M7** measured at 5°C/min.

(iii) A result of X-ray crystallography for [Ir(tpy)$_2$]Br$_3$·7H$_2$O (M7)

Table S1. Crystal data for [Ir(tpy)$_2$]Br$_3$·7H$_2$O **(M7)**

	[Ir(tpy)$_2$]Br$_3$·7H$_2$O
Empirical formula	$C_{30}H_{36}O_7Br_3N_6Ir$
Crystal system	triclinic
Space group	*P*-1 (#2)
Temp. (°C)	-150 ± 1
a (Å)	9.1535(3)
b (Å)	10.7988(2)
c (Å)	18.2428(3)
α (°)	76.4504(15)
β (°)	88.342(2)
γ (°)	87.051(2)
Z	2
V (Å^3)	1750.47(7)
ρ (g/cm^3)	1.944
R_1	0.0552
wR_2	0.1537



[Ir(tpy)$_2$]Br$_3$·7H$_2$O (M7)

Fig. S3. Dihedral angle between the two tpy ligand planes in **M7**. The dihedral angle was calculated between the plane defined by atoms Ir1, C10, C15, and C20 and the plane defined by Ir1, C25, C30, and C35. The tpy ligand planes are shown in red in the figure.

Table S2. Hydrogen bonding parameters for $[Ir(tpy)_2]Br_3\cdot 7H_2O$ **(M7)**

Atom1	Atom2	Length(Å)	Symm. op. 1	Symm. op. 2
Br1	O4	3.366	x,y,z	1-x,1-y,1-z
Br1	O6	3.327	x,y,z	1-x,1-y,1-z
Br2	O1	3.285	x,y,z	1-x,1-y,1-z
Br2	O7	3.32	x,y,z	x,y,z
Br3	O1	3.282	x,y,z	x,y,z
Br3	O3	3.362	x,y,z	1+x,y,z
O1	O2	2.814	x,y,z	x,y,z
O2	O3	2.814	x,y,z	x,y,z
O2	O4	2.751	x,y,z	x,y,z
O4	O5	2.758	x,y,z	1-x,1-y,1-z
O5	O6	2.764	x,y,z	x,y,z

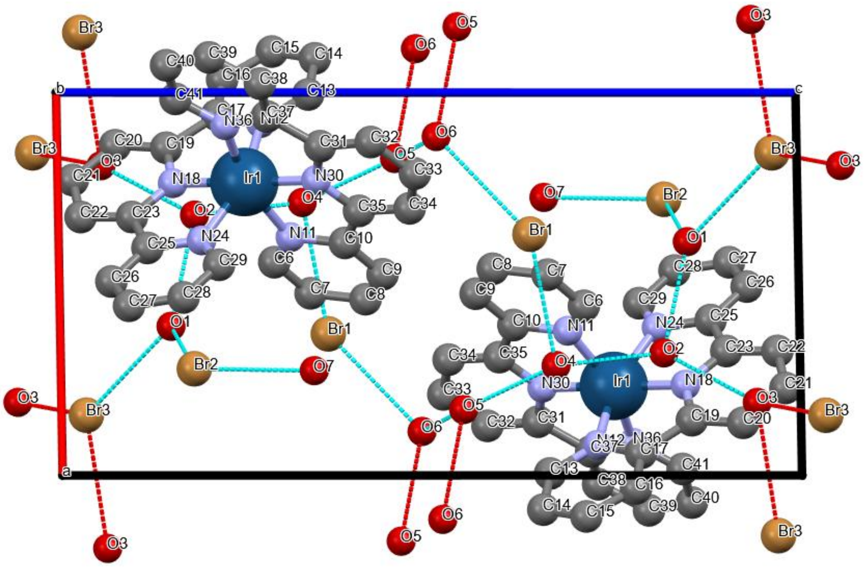


Fig. S4. Hydrogen bond network for $[Ir(tpy)_2]Br_3\cdot 7H_2O$ **(M7).**

(iv) A result of X-ray crystallography for $[Ir(tpy)_2]Br_3 \cdot 2H_2O$ (M2)

Table S3. Crystal data for **$[Ir(tpy)_2]Br_3 \cdot 2H_2O$ (M2)**

	$[Ir(tpy)_2]Br_3 \cdot 2H_2O$
Empirical formula	$C_{30}H_{26}Br_3O_2N_6Ir$
Crystal system	orthorhombic
Space group	$Pna2_1$ (#33)*
Temp. (°C)	-150 ± 1
a (Å)	9.72848(19)
b (Å)	16.4054(3)
c (Å)	18.5653(4)
α (°)	90
β (°)	90
γ (°)	90
Z	4
V (Å^3)	2963.01(10)
ρ (g/cm^3)	2.095
R_1	0.0257
wR_2	0.0525

**CIFcheck suggested the possibility of the Pnna space group; therefore, refinement was also performed in Pnna. However, the tpy ligand had to be modeled as disordered, many atoms showed non-positive definite or abnormally small displacement parameters, and the R factor (R1 ≈ 15%) was significantly higher than that for $Pna2_1$ (R1 = 2.57%). These results indicate that $Pna2_1$ is the more appropriate space group for this structure.*

Table S4. Crystal data for **$[Ir(tpy)_2]Br_3 \cdot 2H_2O$ (M2)**

Atom1	Atom2	Length(Å)	Symm. op. 1	Symm. op. 2
Br40	O42	3.358	x,y,z	1-x,1-y,1/2+z
O41	Br39	3.355	x,y,z	2-x,1-y,1/2+z

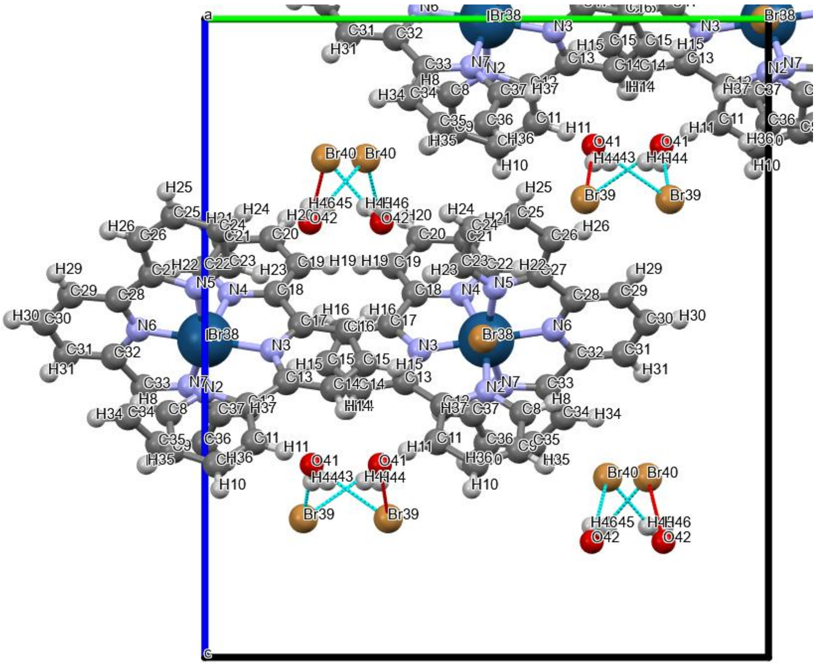


Fig. S5. Hydrogen bond network for $[Ir(tpy)_2]Br_3\cdot 2H_2O$ **(M2).**

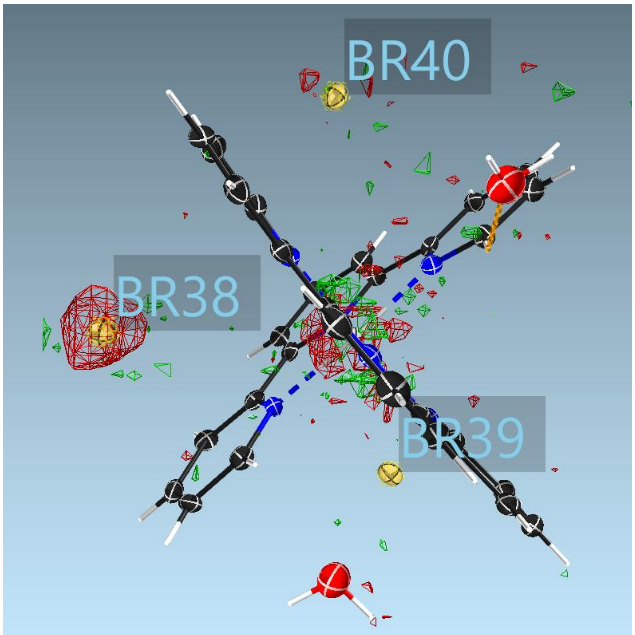


Fig. S6. Electron density depletion in Br38 for $[Ir(tpy)_2]$ $Br_3\cdot 2H_2O$ (**M2**).
Red and green isosurfaces indicate negative and positive residual electron densities, respectively.

(v) Simulation of PXRD patterns for M7 and M2

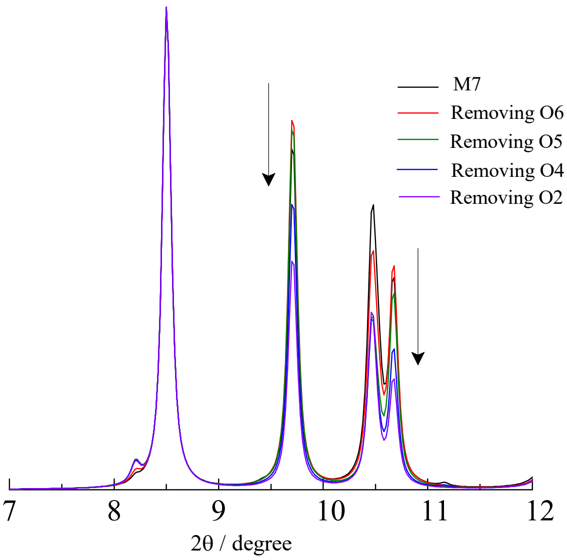


Fig. S7. Simulations of PXRD patterns for **M6**–**M3** removed H_2O one by one from atomic coordinates in CIF of M7. The peaks at 2q = 8.5°. are normalized. The simulation patterns are produced by using Mercury. [s1]

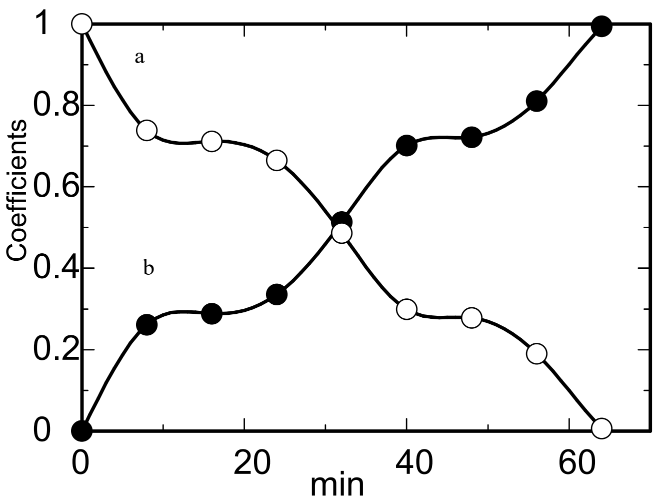


Fig. S8. Plots of coefficients (*a* and *b*) obtained for the simulations of PXRD patterns during the transition from **M2** to **M7** using $I = aI(\mathbf{M2}) + bI(\mathbf{M7})$. I(**M2**) and I(**M7**) are simulated patterns for **M2** and **M7**, respectively.

(vi) PXRD results for M7, M2, M1, M0

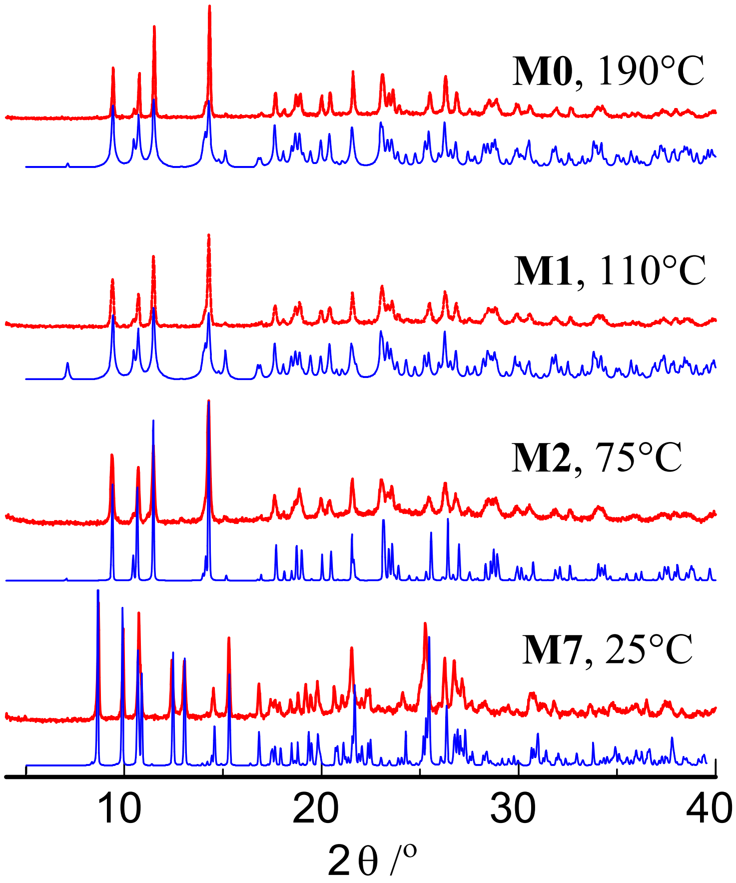


Fig. S9. PXRD patterns (red) and their simulation (blue) for $[Ir(tpy)_2]Br_3 \cdot nH_2O$ (**Mn**, n = 7, 2, 1, 0). The simulations of **M2** and **M7** are produced from the results of single crystal X-ray diffraction analysis using Mercury program[s1] and those of **M1** and **M0** are predicted by using Rietan program.[s2]

Table S5 Lattice parameters predicted by the Rietveld analysis using the Rietan program.[s2]

	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*V* ($Å^3$)
M2 (75°C)	9.82917	16.5294	18.7986	90.0	90.0	90.0	3054.21
M1 (110°C)	9.81466	16.5161	18.7709	90.0	90.0	90.0	3042.76
M0 (190°C)	9.81552	16.4899	18.7783	90.0	90.0	90.0	3039.4

(vii) Emission spectrum of M7 at 77K

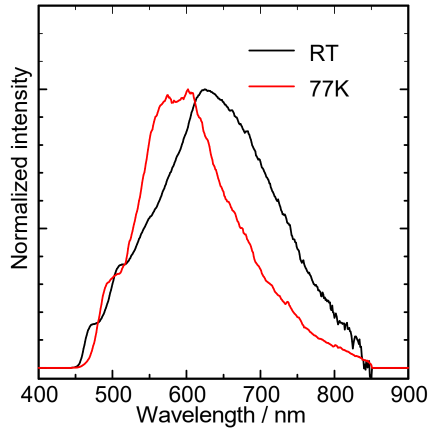


Fig. S10. Emission spectrum (red) of **M7** at 77 K is blue shifted compared with that at RT. Although the emission intensity is enhanced at 77 K, a shoulder assignable the p-p* emission is still observed at around 500 nm.

(viii) Emission lifetime of M7 and M2

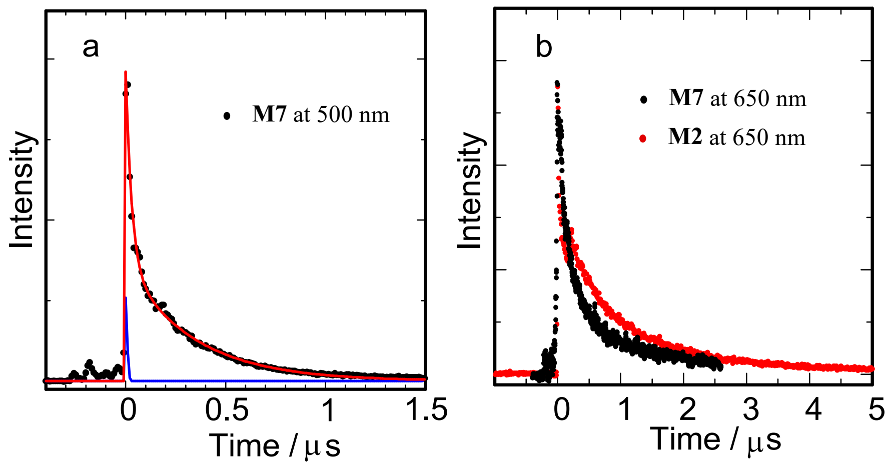


Fig. S11. (a) An emission time-course of **M7** (black dots) monitored at 500 nm consisting of fast and slow decays. The red line is the best fit using a double exponential function. The slow component of emission lifetime is determined as τ = 300 ns, while the fast component is estimated to be 20 ns. The blue line is the pulse profile of N_2 laser with FWHM of ca. 20 ns. (b) Emission decay curves of **M2** (red dots) and **M7** (black dots) monitored at 650 nm after the N_2 laser excitation. The emission lifetimes of **M2** and **M7** are τ = 860 ns and 540 ns, respectively.

(ix) Vapchromic behaviours for the M7–M2 system

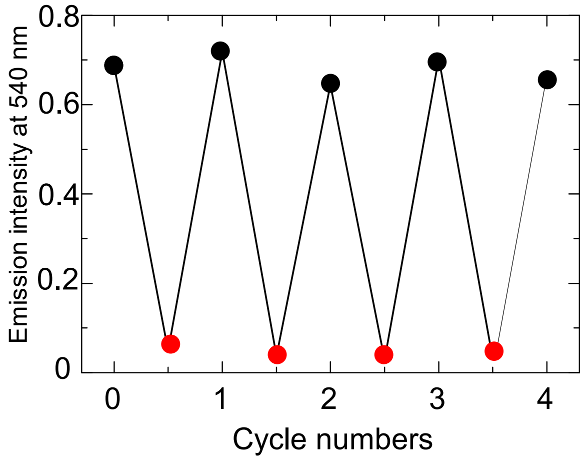


Fig. S12. A plot of emission intensities at 540 nm, the emission peak wavelength of $[Ir(tpy)_2]Br_3 \cdot 7H_2O$. Black and red circles are peak intensities observed upon heating at 80°C and cooling at room temperature, respectively.

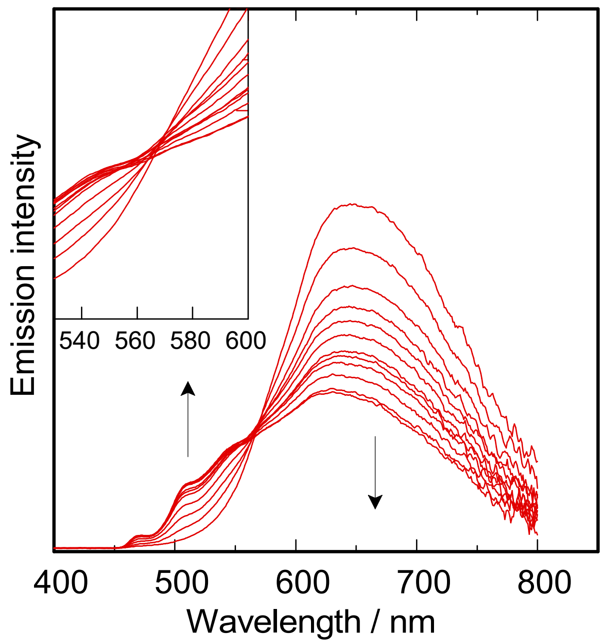


Fig. S13. A change in emission spectrum of **M2** during the cooling at room temperature. While the broad spectrum decreases and the structured spectrum grows with an iso-emissive point at around 570 nm at the beginning, the iso-emissive point disappears gradually (inset).

(x) Vapochromic behaviours for the M2-M0 system

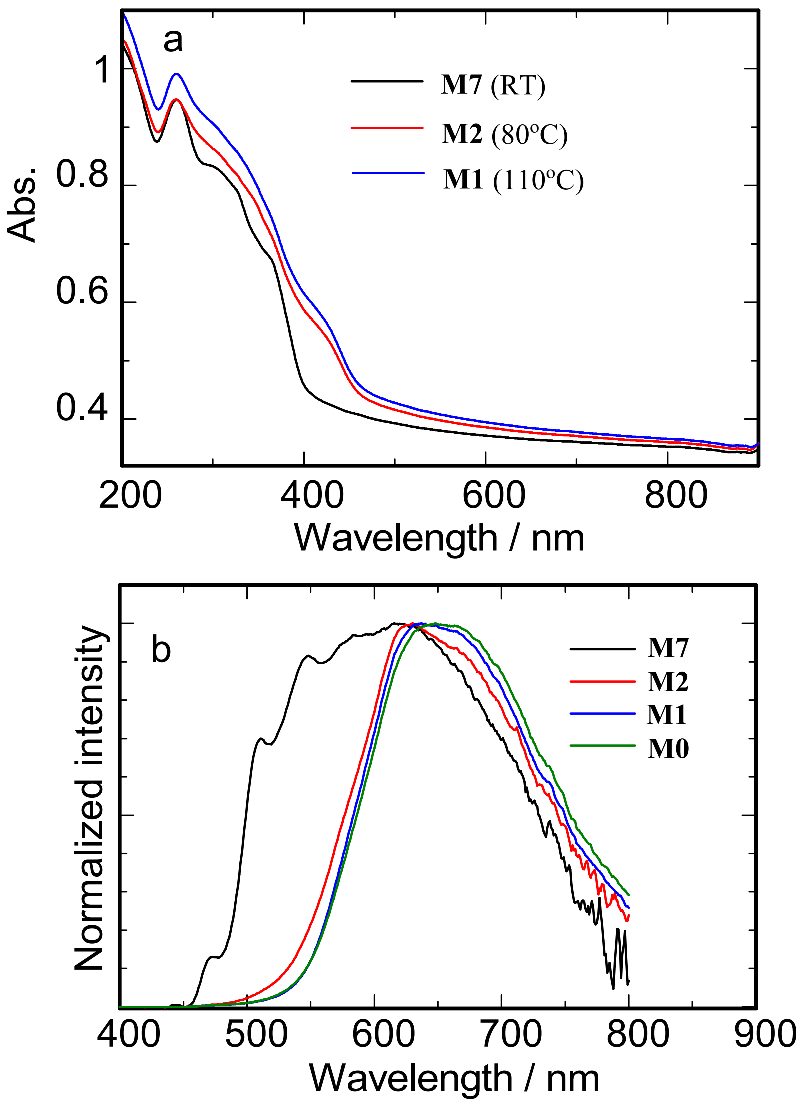


Fig. S14. UV-vis absorption (a) and emission (b) spectra of **M7**, **M2**, **M1**, **M0**

(xi) Reference

s1. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453–457.

s2. F. Izumi and K. Momma, *Solid State Phenom.*, 2007, **130**, 15–20.