Supplementary Information

for

Vapochromic luminescence of a spin-coated copper(I) complex thin film by the direct coordination of vapour molecules

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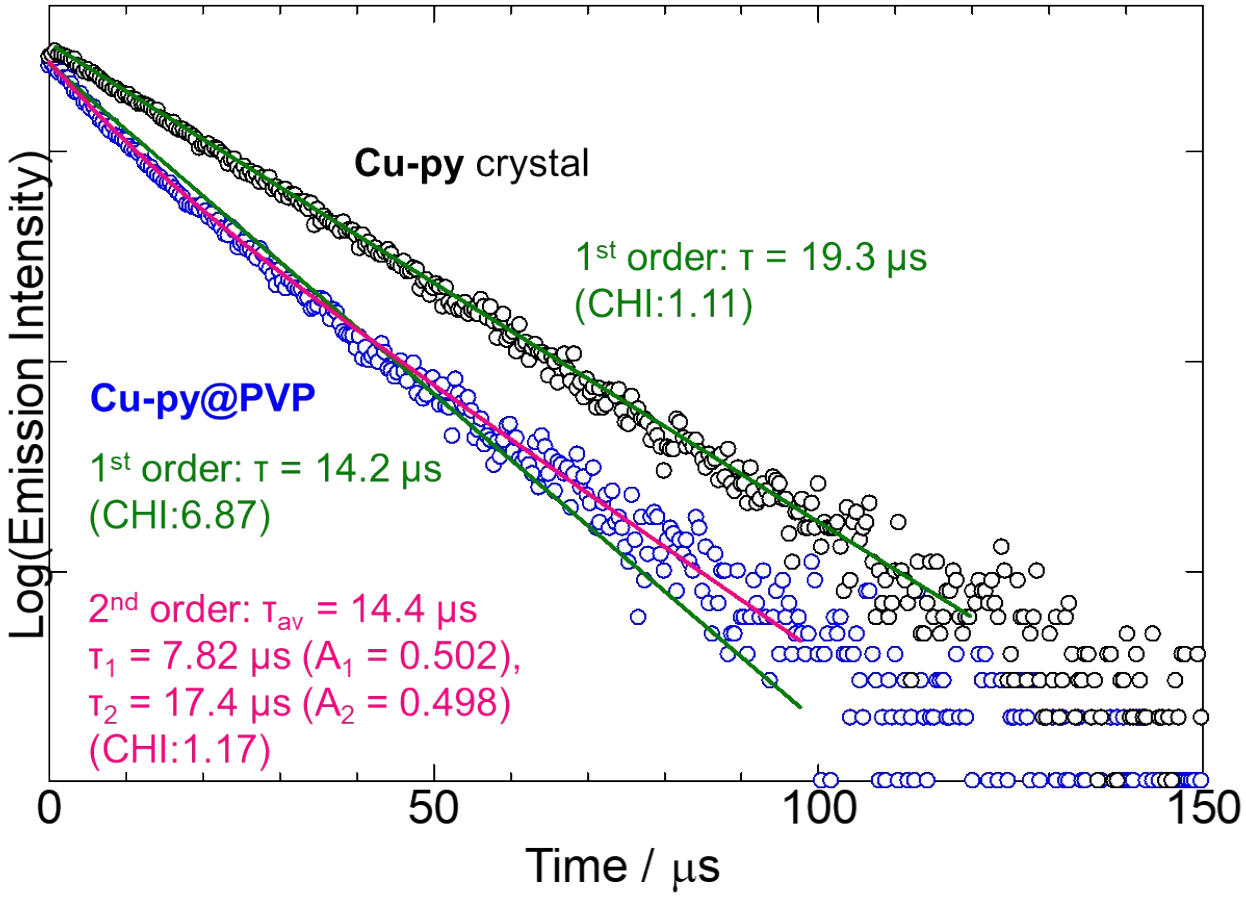

Fig. S1 Emission decays of **Cu-py@PVP** (blue) and **Cu-py crystal** (black) (at 298 K, λ_{ex} = 337 nm).

Green and pink lines show the 1st and 2nd order fitting curves, respectively.

The 2nd order fitting: $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. CHI = value of the χ^2 test.

The average emission lifetime: $\tau_{av} = \Sigma A_i\tau_i^2 / \Sigma A_i\tau_i$ (i = 1, 2).

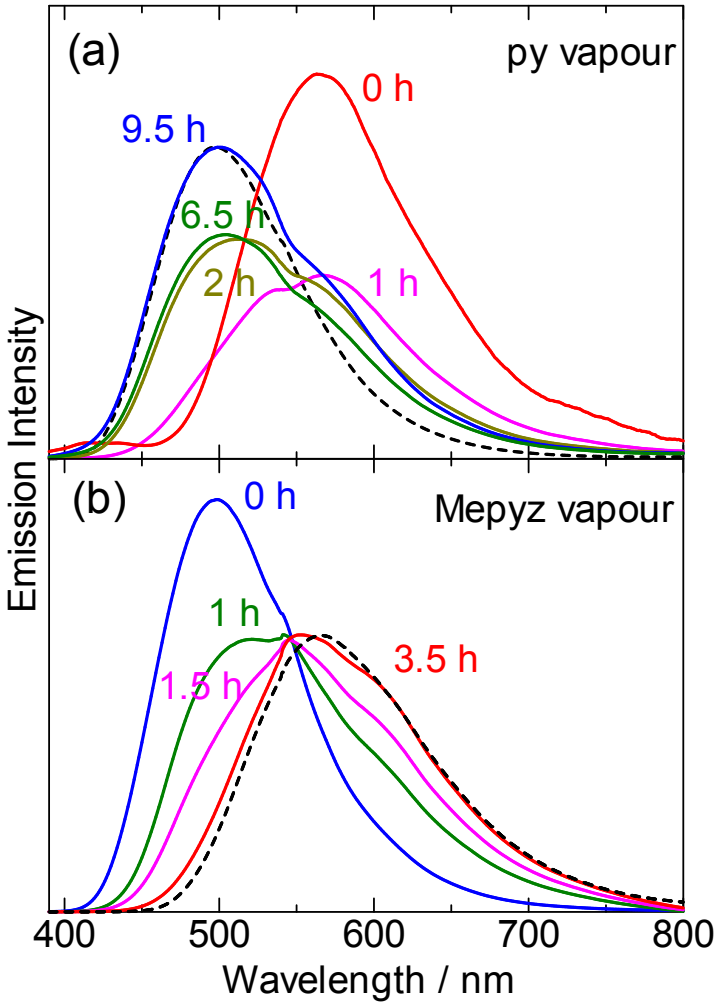

Fig. S2 Changes of emission spectra (λ_{ex} = 350 nm) of (a) **Cu-Mepyz** and (b) **Cu-py** on exposure to py and Mepyz vapour, respectively at 298 K. Each black dashed line in both panels shows the emission spectrum of (a) **Cu-py** and (b) **Cu-Mepyz**.

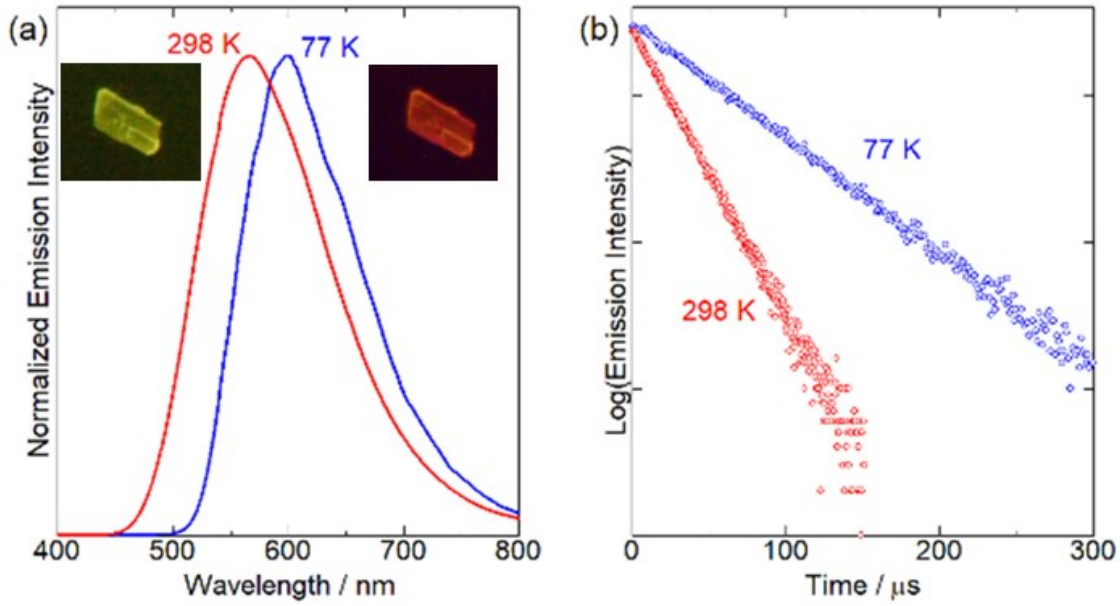

Fig. S3 (a) Emission spectra of **Cu-Mepyz** (solid, λ_{ex} = 350 nm) and (b) emission decays of **Cu-Mepyz** (solid, λ_{ex} = 337 nm) at 298 K (red) and 77 K (blue). Inset in (a) is the photos of **Cu-Mepyz** under UV light irradiation. Photophysical Data at 298 and 77 K: λ_{max} = 566, 598 nm; τ = 22.5, 55.4 μs; Φ = 0.94, 0.77. The numerical data at 298 K are also included in Table 1.

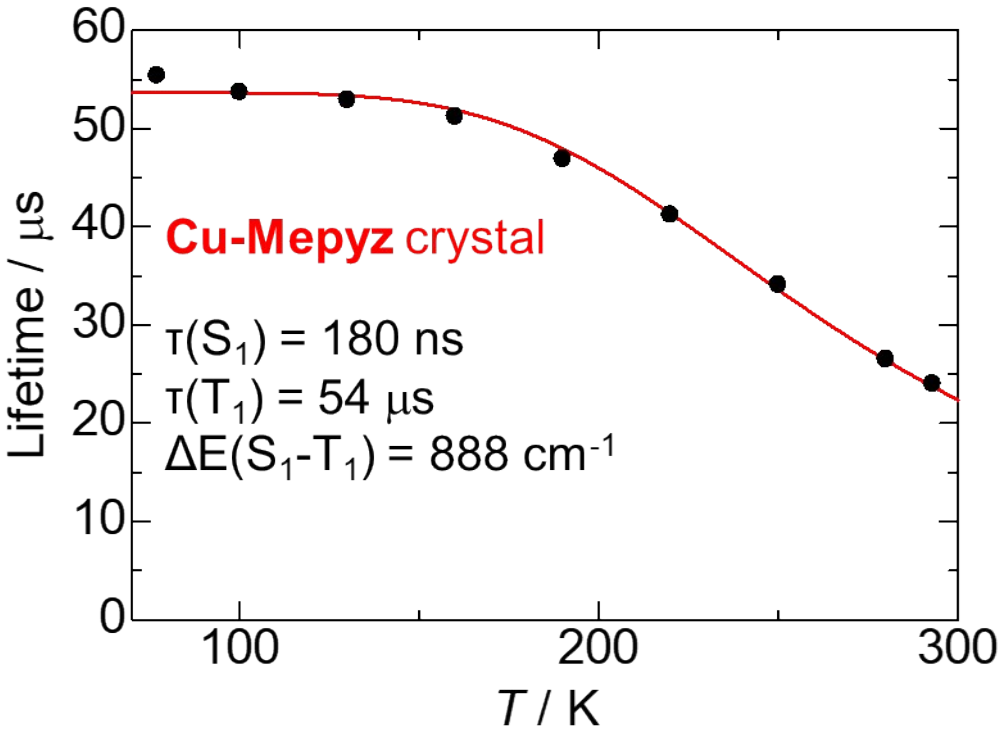

Fig. S4 Temperature dependence of the emission lifetime of **Cu-Mepyz** in the solid state (λ_{ex} = 337 nm). The red line is a calculated one from eq 1 based on the two-state (S_1 and T_1) model,[S1]

$$\tau(T) = \frac{3 + exp\left[-\frac{\Delta E}{RT}\right]}{\frac{3}{\tau(T_1)} + \frac{1}{\tau(S_1)} exp\left[-\frac{\Delta E}{RT}\right]} \qquad (eq\ 1)$$

where ΔE is the energy difference between the singlet (S_1) and triplet (T_1) states, $\tau(S_1)$ and $\tau(T_1)$ are the lifetimes of the S_1 (fluorescence) and T_1 (phosphorescence) states, R is the ideal gas constant, and T is the absolute temperature.

S1. (a) M. J. Leitl, F. -R. Küchle, H. M. Mayer, L. Wesemann and H. Yersin, *J. Phys. Chem. A*, 2013, **117**, 11823–11826. (b) H. Ohara, A. Kobayashi and M. Kato, *Dalton Trans.,* 2014, **43,** 17317–17323.

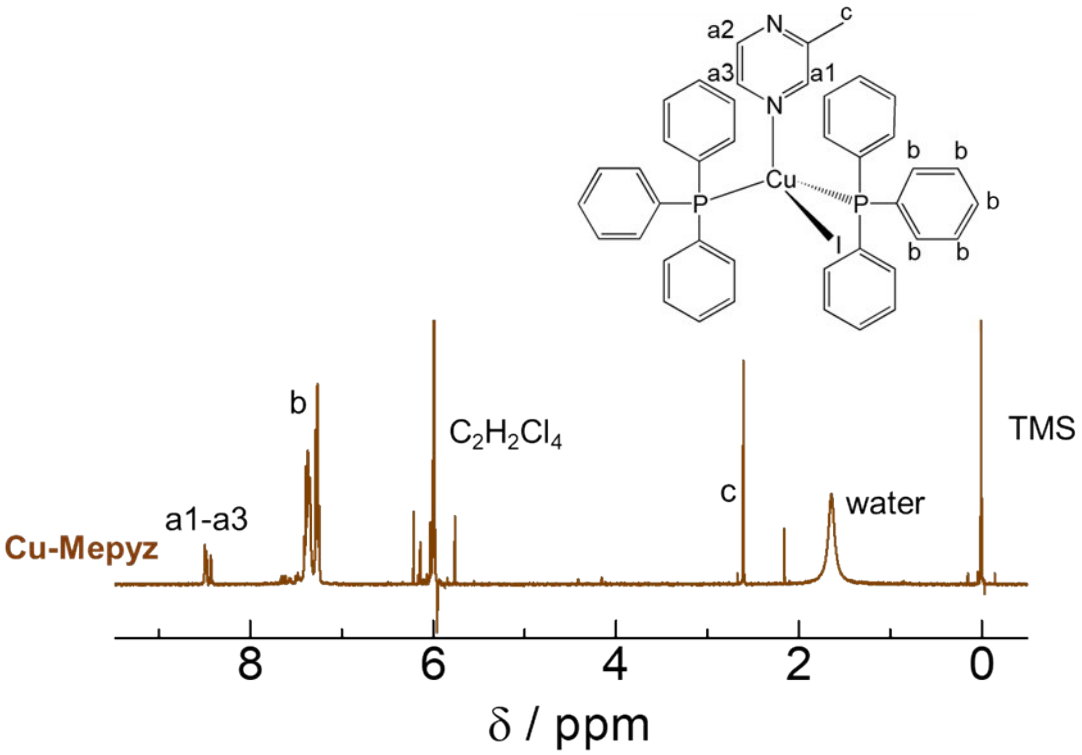

Fig. S5 ^{1}H NMR spectrum of the **Cu-Mepyz** crystal (400 MHz, $C_2D_2Cl_4$, 293 K).

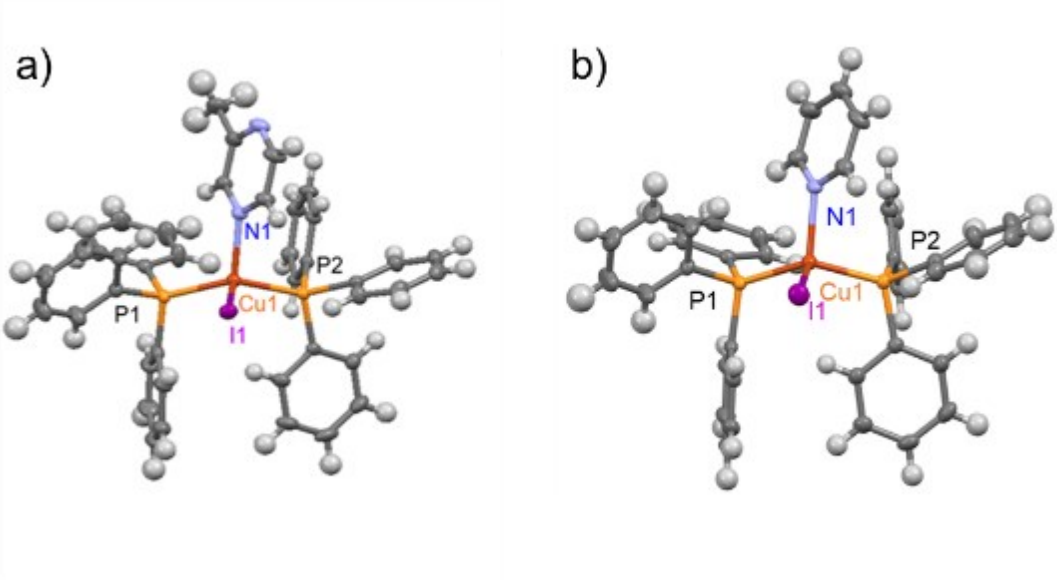

Fig. S6 Molecular structures of (a) **Cu-Mepyz** and (b) **Cu-py** with thermal vibrational ellipsoids at the 50% probability level.

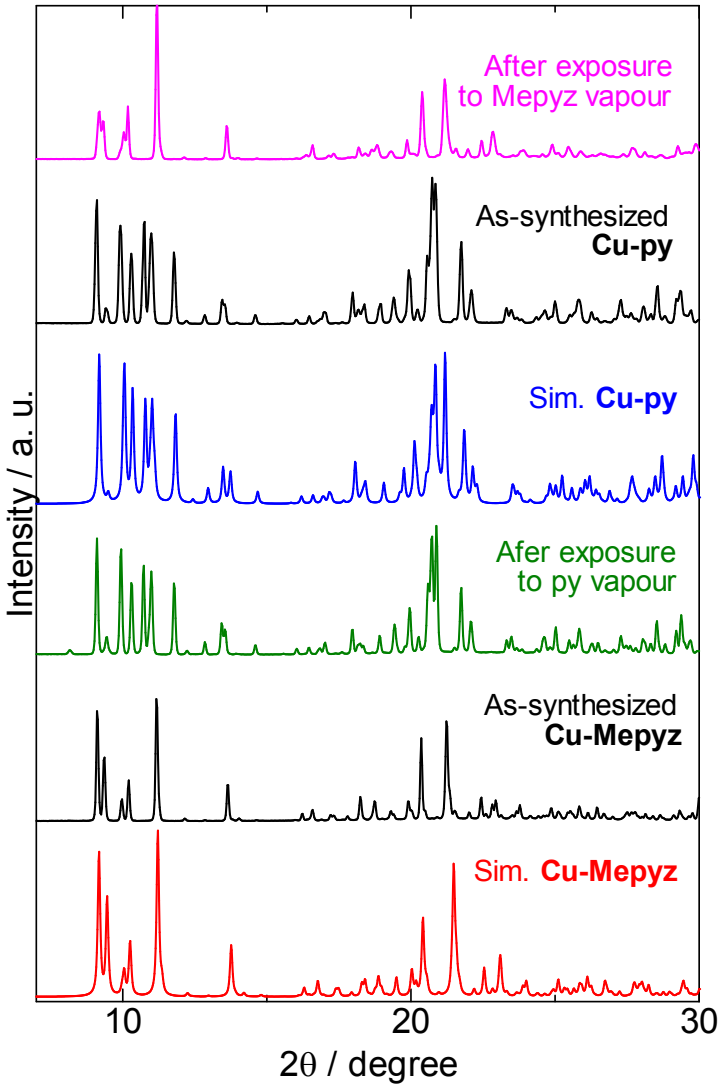

Fig. S7 Changes of PXRD patterns of **Cu-Mepyz** and **Cu-py** under exposure to py and Mepyz vapour respectively at 298 K. Red and blue lines are the simulation patterns calculated from the crystal structures of **Cu-Mepyz** and **Cu-py**, respectively.

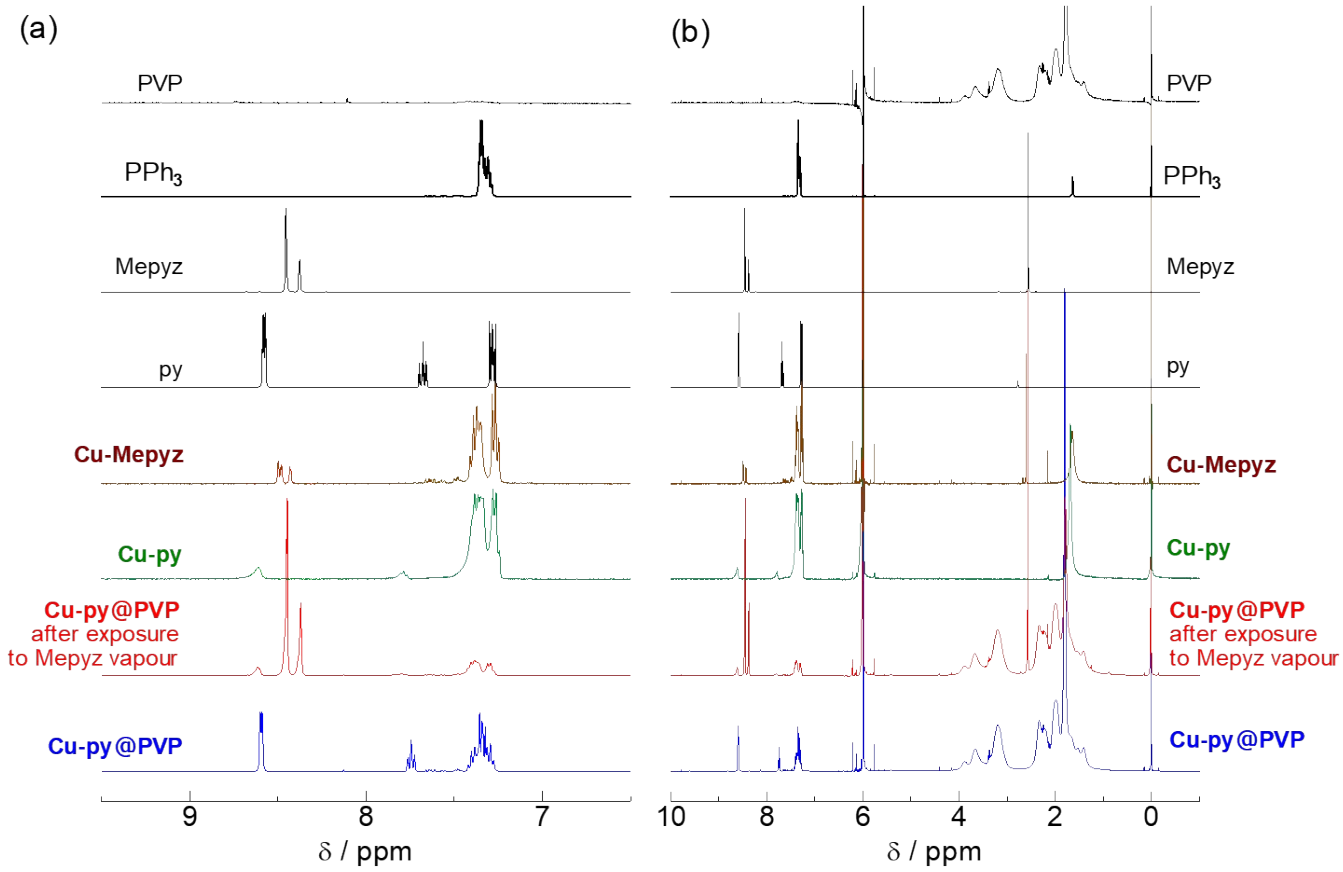

Fig. S8 Changes of ^{1}H NMR spectrum in (a) aromatic region and (b) whole range of **Cu-py@PVP** before (blue) and after (red) exposure to Mepyz vapour (293 K, 400 MHz, in $C_2D_2Cl_4$). The spectral measurements were done for the solutions obtained by dissolving the film samples in $C_2D_2Cl_4$. The top five lines are the spectra of PVP polymer, PPh_3, Mepyz, py, **Cu-Mepyz**, and **Cu-py** in $C_2D_2Cl_4$.

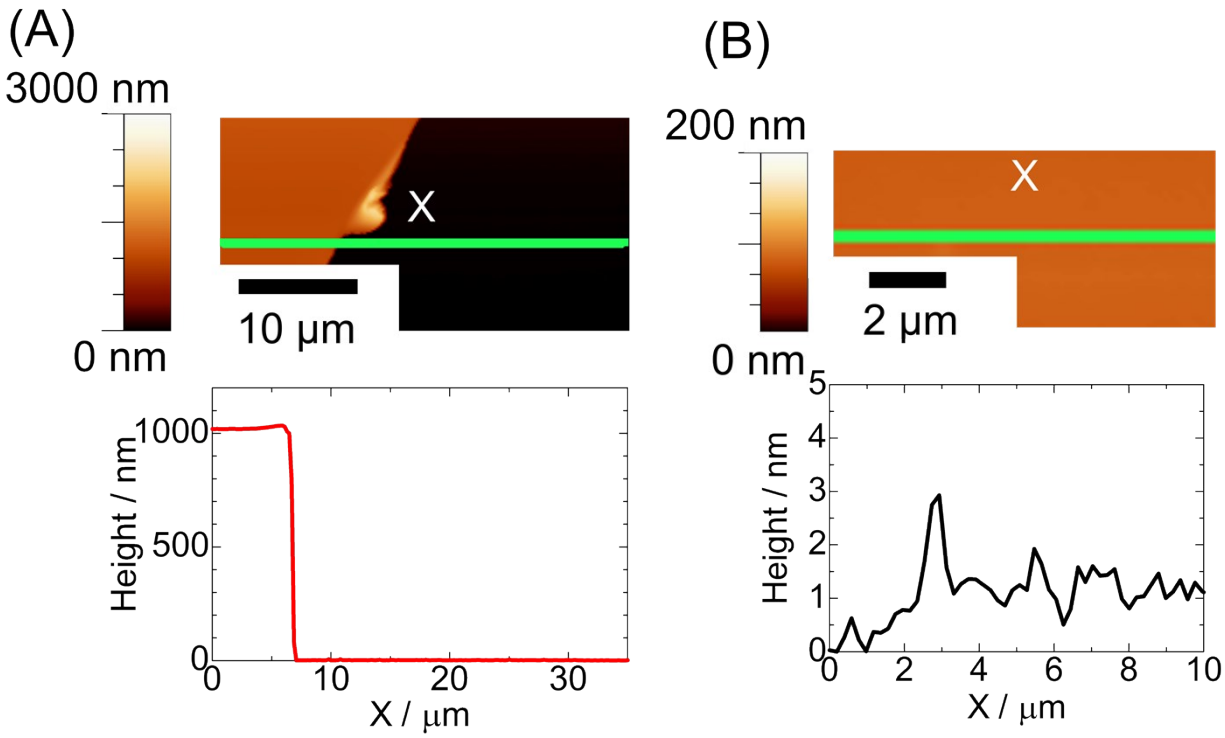

Fig. S9 AFM images (top) and the height profile (bottom) of the surface of (A) the boundary area scratched **Cu-py@PVP** after exposure to Mepyz vapour and (B) Enlarged surface of **Cu-py@PVP** after exposure to Mepyz vapour.

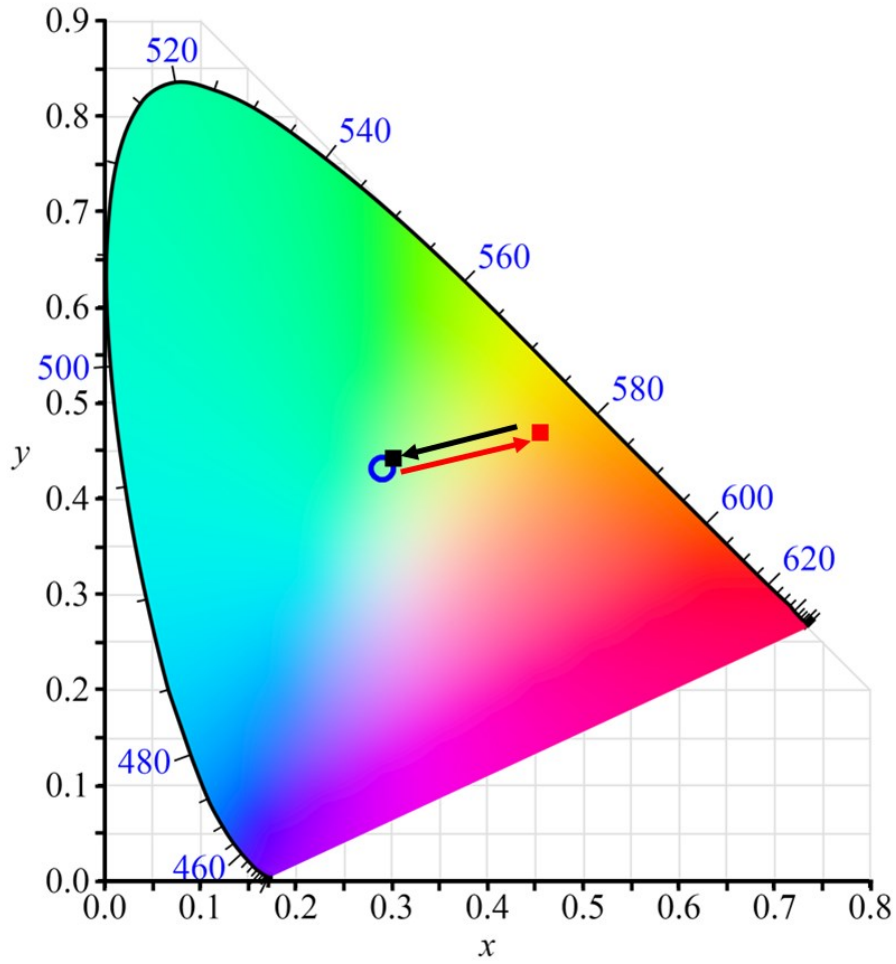

Fig. S10 Change of Chromaticity color coordinate plots for **Cu-py@PVP** (blue circle) after exposure to Mepyz vapour (red square) and the subsequent exposure to py vapour (black square).

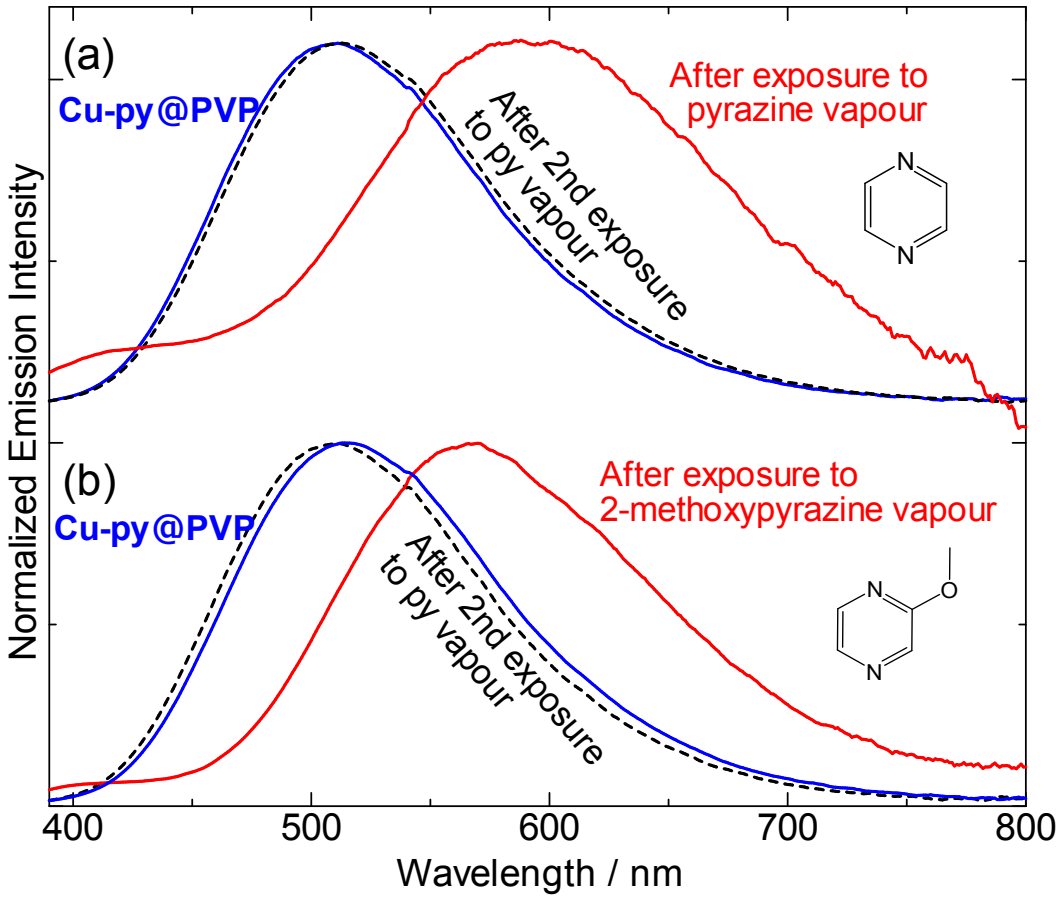

Fig. S11 Changes of emission spectra of **Cu-py@PVP** (blue lines) before and (red lines) after exposure to (a) pyrazine and (b) 2-methoxypyrazine vapour for 2 min (298 K, λ_{ex} = 350 nm). Black dotted lines are the spectra of the films after the subsequent exposure to py vapour for 2 min to recover the original **Cu-py@PVP**.

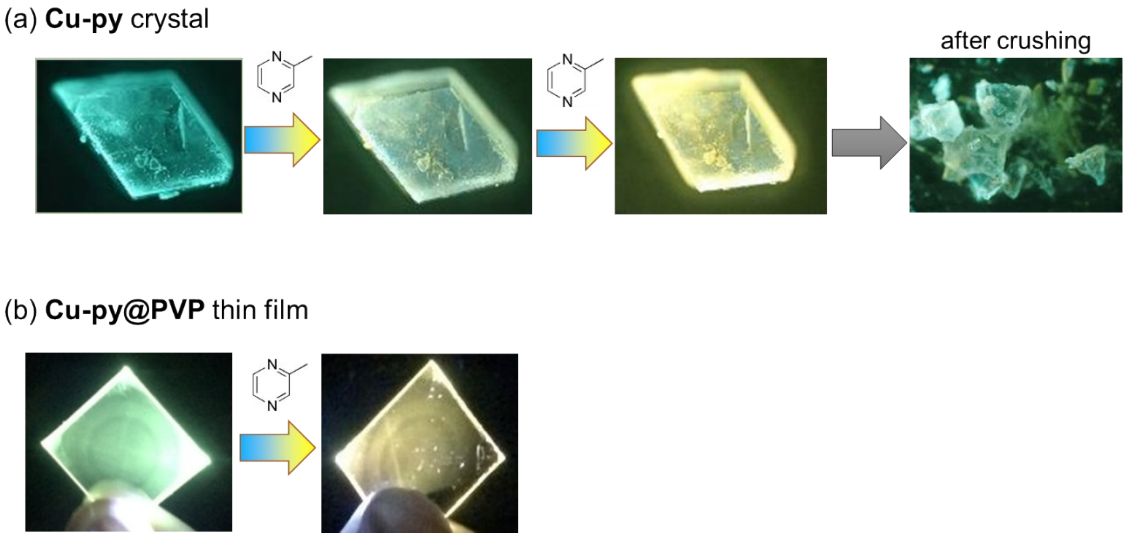

Fig. S12 Photographs showing the luminescence changes for (a) **Cu-py** crystal and (b) **Cu-py@PVP** under exposure to Mepyz vapour. The right-side image in (a) is the photograph of crushed crystals after exposure to Mepyz vapour.

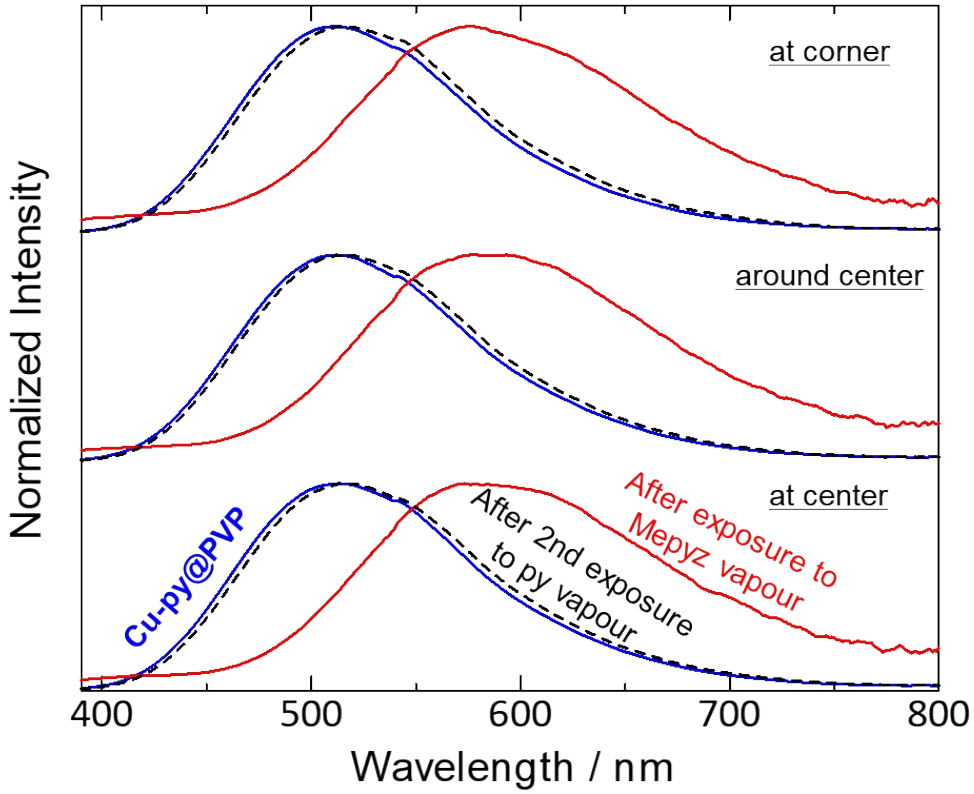

Fig. S13 Changes of emission spectra (λ_{ex} = 350 nm) at several different positions on **Cu-py@PVP** (blue lines) after exposure to Mepyz vapour (red line) and the subsequent exposure to py vapour (black dash line).

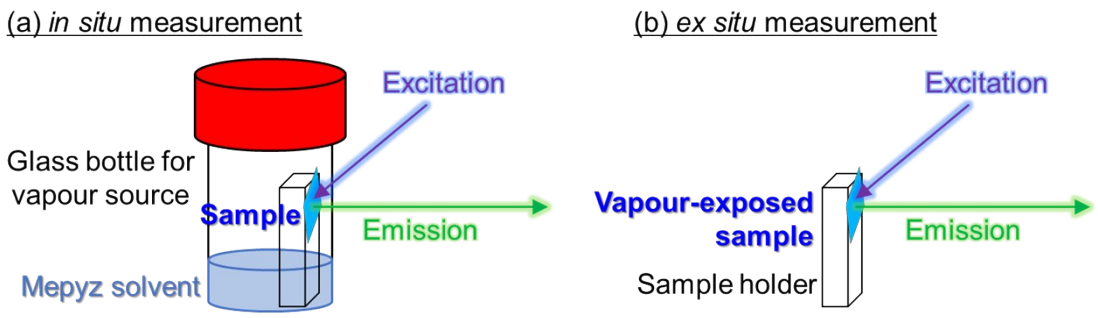

Fig. S14 Schematic images of the experimental setup for (a) *in-situ* emission spectral measurement under vapour exposure and (b) *ex-situ* measurement for the vapour-exposed sample.

Table S1 Crystal parameters and refinement data of **Cu-Mepyz** compared with **Cu-py**.

Complex	**Cu-Mepyz**	**Cu-py**
T / K	150	150
Formula	$C_{41}H_{36}CuIN_2P_2$	$C_{41}H_{35}CuINP_2$
Formula weight	809.10	794.08
Crystal system	*monoclinic*	*triclinic*
Space group	$P2_1/c$	P-1
a / Å	9.7754(1)	9.8484(2)
b / Å	37.378(3)	10.4600(2)
c / Å	10.999(1)	19.4312(4)
α / °	90	82.078(1)
β / °	115.013(1)	85.532(2)
γ / °	90	63.583(2)
V / Å ^{3}	3642.08(6)	1775.26(7)
Z	4	2
D_{cal} / g cm^{-3}	1.476	1.486
Reflections collected	20824	19616
Unique reflections	15531	13802
R_{int}	0.0255	0.0250
GOF	1.046	1.151
R_1 ($I > 2\sigma(I)$) [a]	0.0256	0.0308
wR_2 [b]	0.0683	0.1292

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o)^2]^{1/2}$, $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 - 2F_c^2)/3$.

Table S2 Selected bond lengths (Å) and angles (°) of **Cu-Mepyz** compared with **Cu-py**.

	Cu-Mepyz	**Cu-py**
Cu1-I1	2.625(3)	2.636(4)
Cu1-P1	2.274(1)	2.273(7)
Cu1-P2	2.278(2)	2.279(7)
Cu1-N1	2.107(2)	2.124(4)
I1-Cu1-P1	103.0(2)	102.8(2)
I1-Cu1-P2	113.0(2)	108.8(2)
I1-Cu1-N1	103.0(5)	108.7(8)
P1-Cu1-P2	125.0(3)	126.0(3)