Supplementary Information

for

Vapoluminescent thin-film with unsaturated copper(I) complex for rapid light-on sensing of N-heteroaromatic vapour

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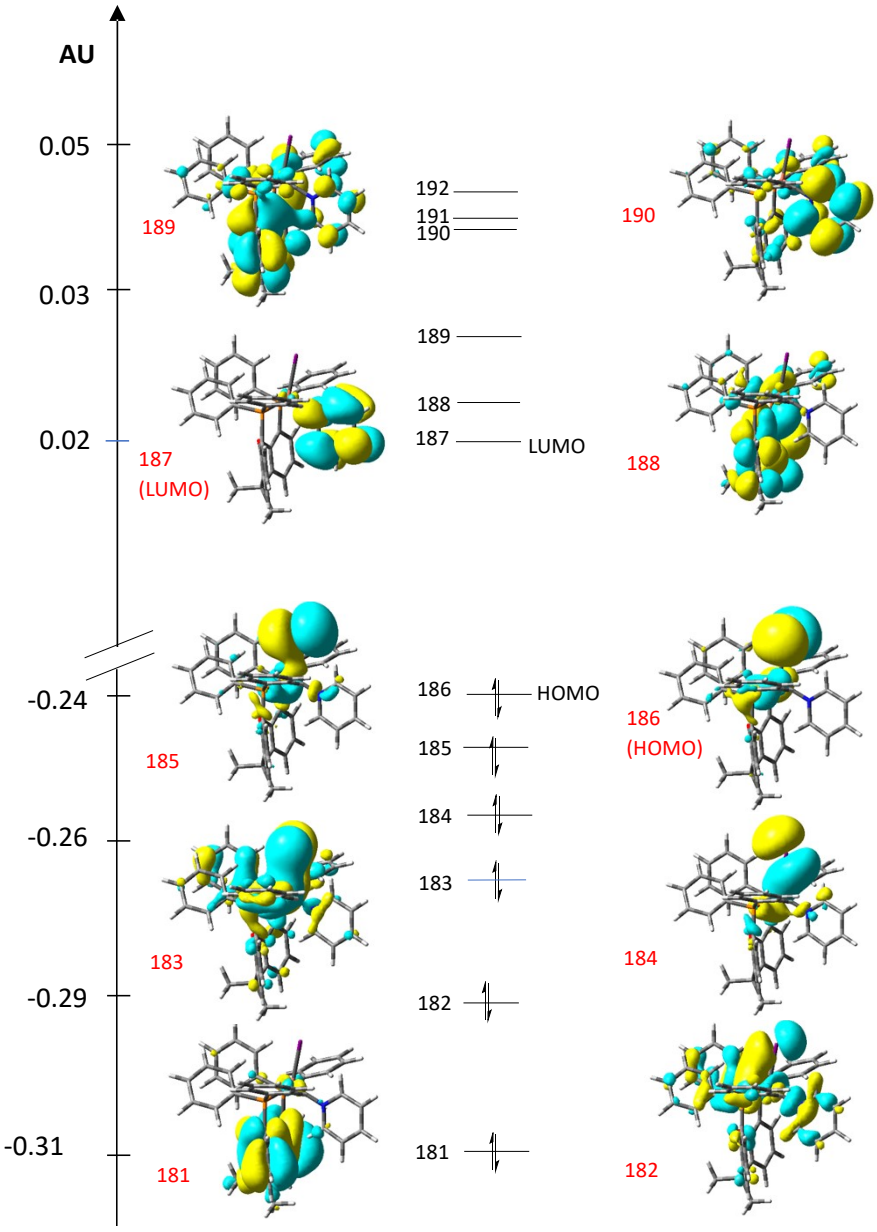


Fig. S1 Kohn-Sham frontier orbitals of the optimized ground state (S_0) of **Cu-x-py**. (iso value = 0.02)

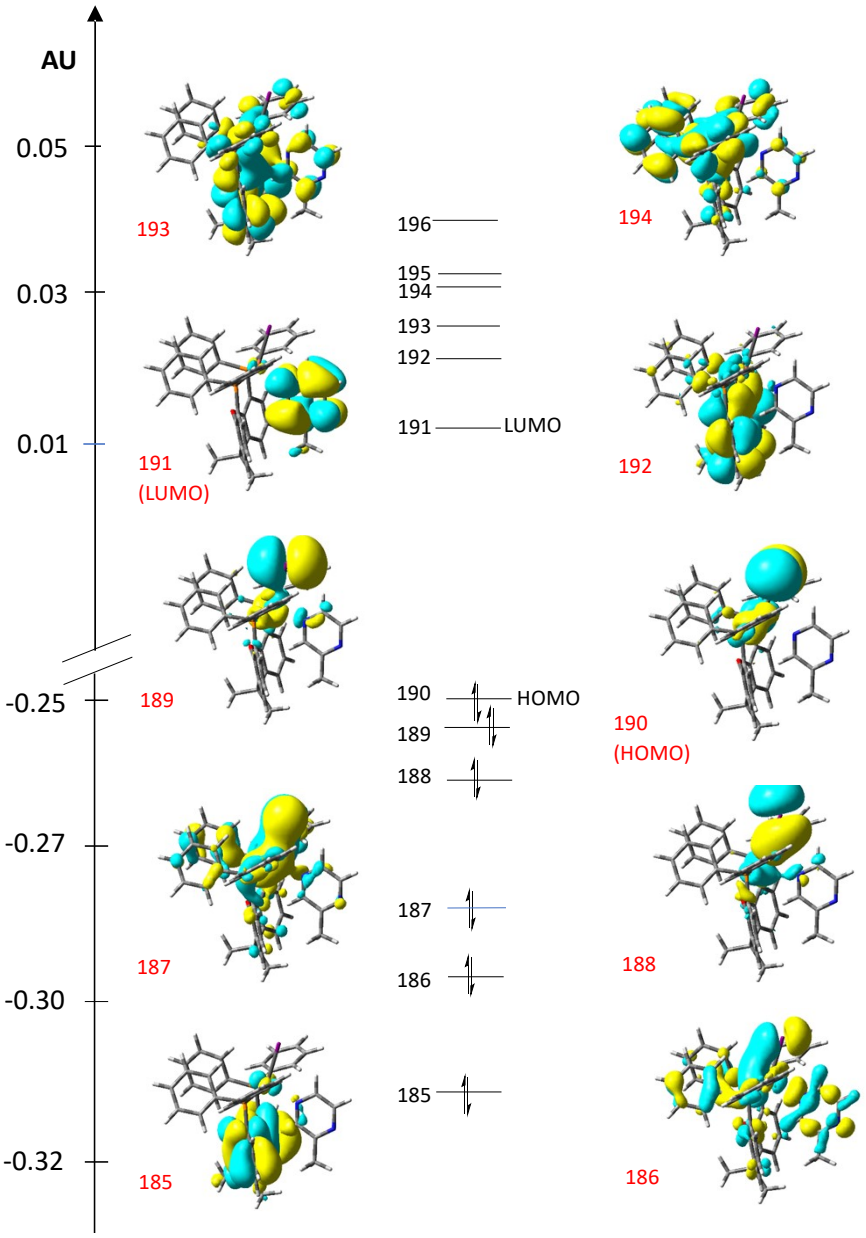


Fig. S2 Kohn-Sham frontier orbitals of the optimized ground state (S_0) of **Cu-x-Mepyz**. (iso value = 0.02)

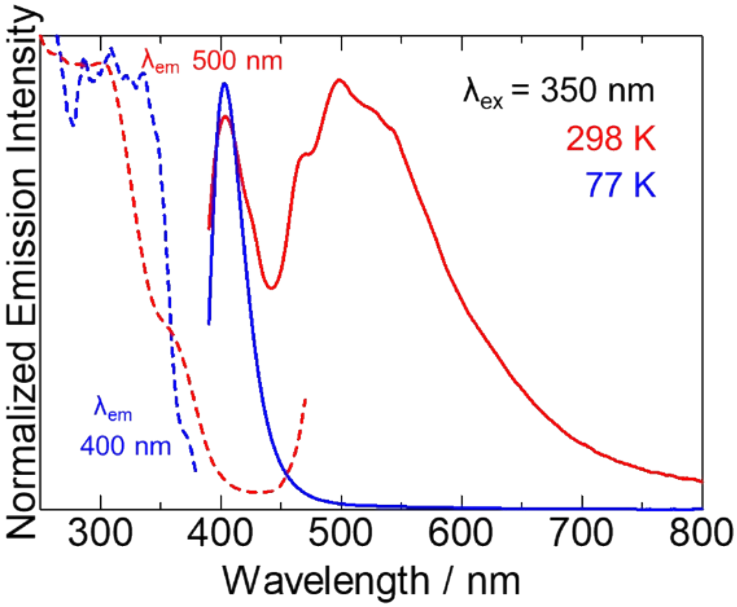


Fig. S3 Emission and excitation spectra of **Cu-x** in the solid state. (λ_{ex} = 350 nm at 298 and 77 K).

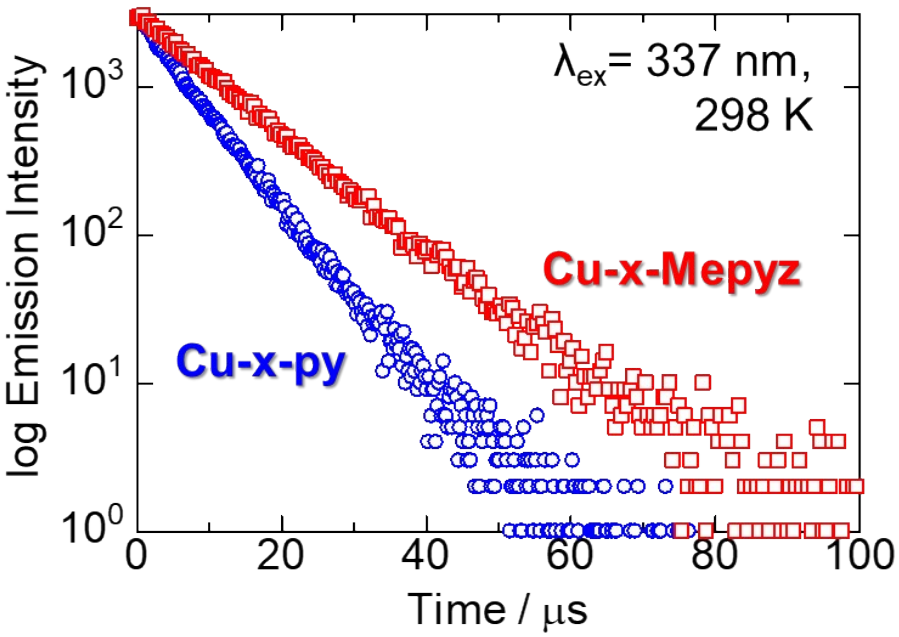
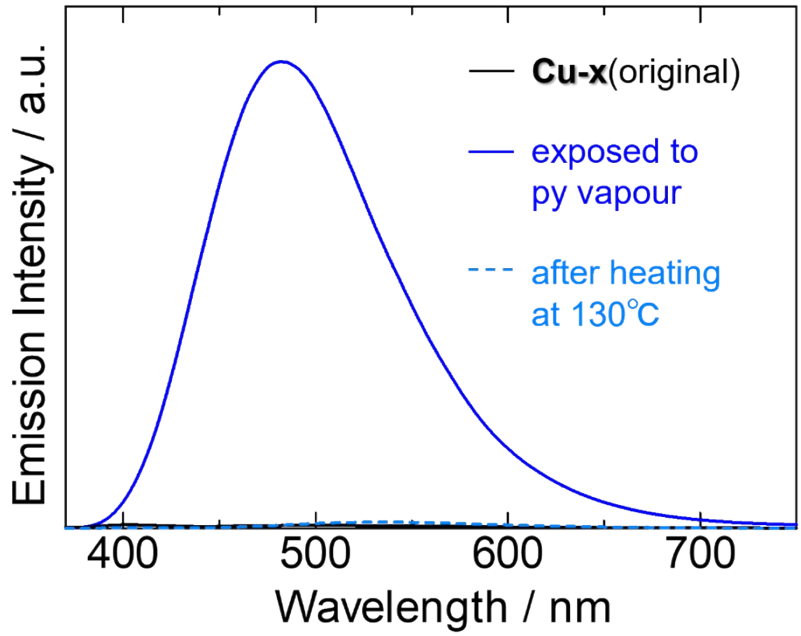
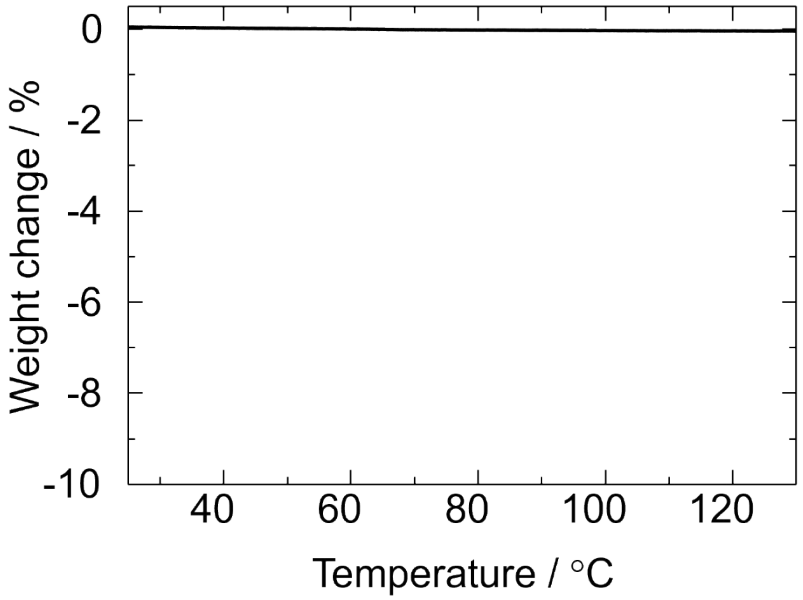


Fig. S4 Emission decay of (a) **Cu-x-py** crystal and (b) **Cu-x-Mepyz** crystal (λ_{ex} = 337 nm, at 298 K).



(a)



(b)

Fig. S5 (a) Emission spectral changes of **Cu-x** powder before and after py vapour exposure and after the subsequent heating at 130 °C (λ_{ex} = 350 nm, at 298 K). (b) TG diagram of the sample after heating at 130 °C (5 °C / min under Ar flow). No weight change was observed indicating that the py molecules have already been lost completely from the sample.

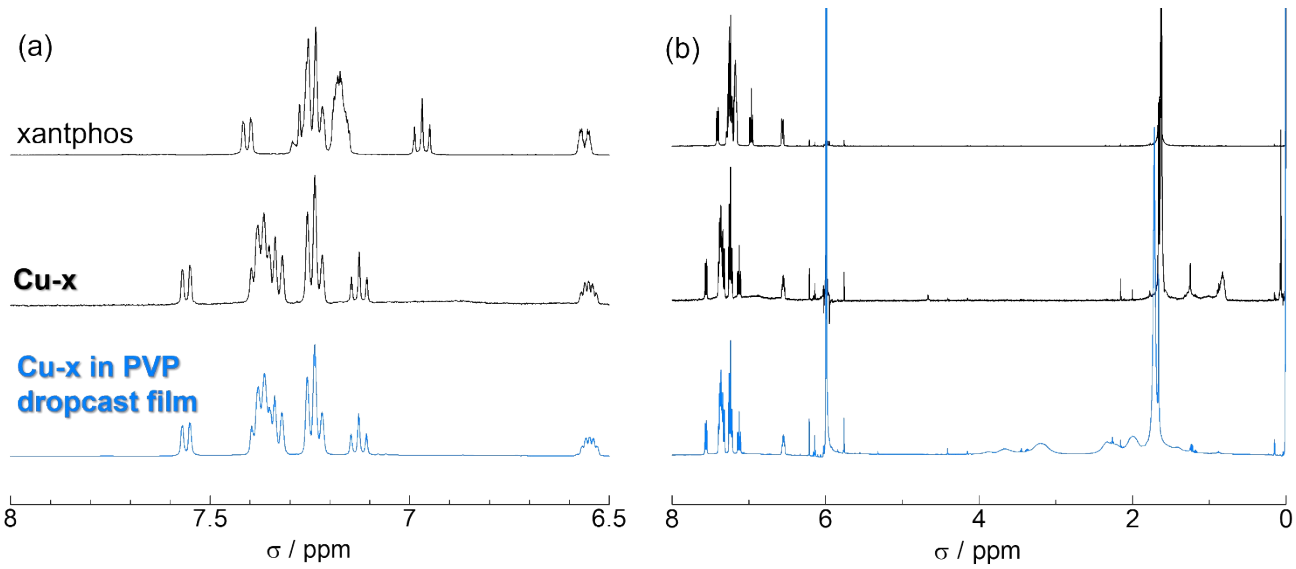


Fig. S6 ^{1}H NMR spectra of **Cu-x** in drop-cast PVP film (blue line), (a) the aromatic region and (b) the whole range (at 293 K, 400 MHz, in 1,1,2,2-Tetrachloroethane-d_2). Those of xantphos and **Cu-x** are shown for comparison.

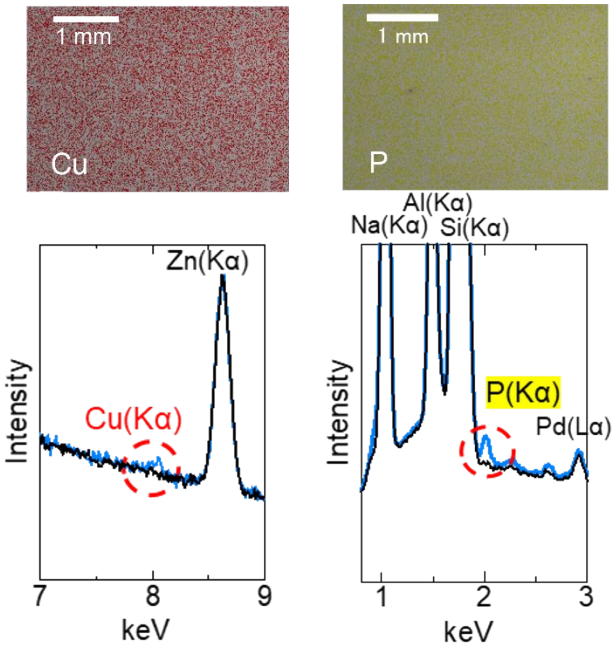


Fig. S7 EDX elemental mapping images of Cu and P (upper) and EDX spectra at Cu K-edge (left) and P K-edge (right) (lower, blue lines) for **Cu-x@PVP** surface on ITO slide glass. Black lines show those of the PVP film.

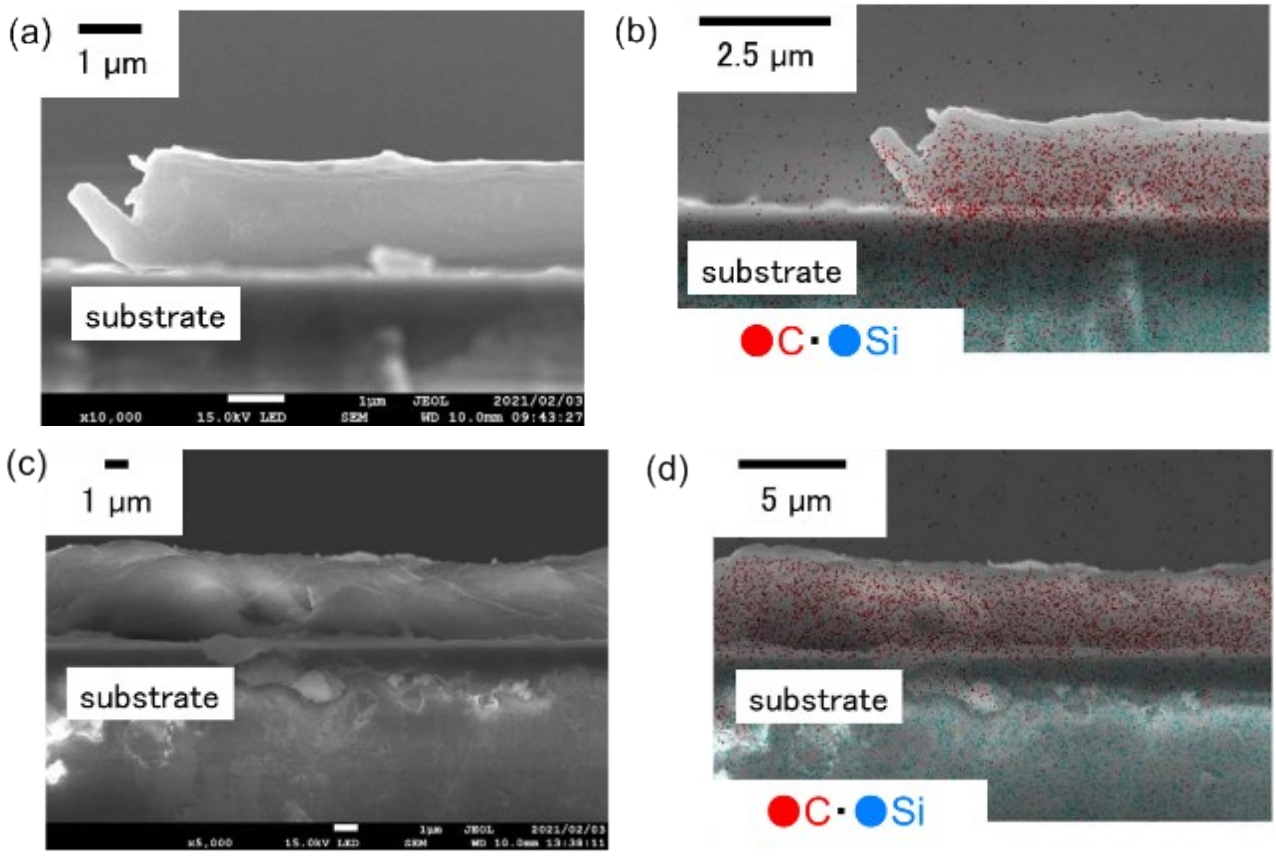


Fig. S8 Cross section SEM images of (a) **Cu-x@PVP** and (c) **Cu-x-py@PVP** and cross section elemental mappings of (b) **Cu-x@PVP** and (d) **Cu-x-py@PVP**.

The cross section generated when the substrate was divided in half was observed.

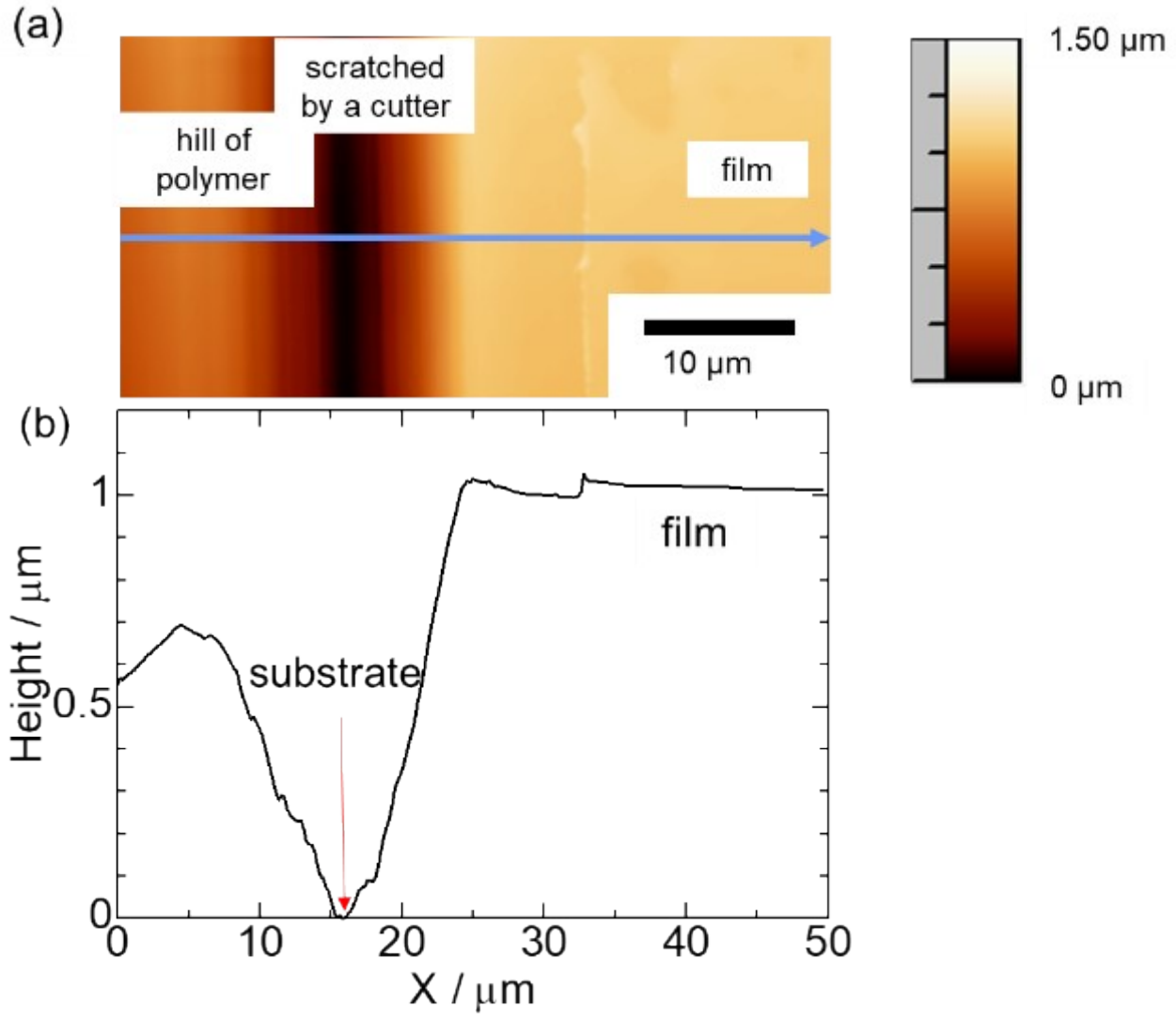


Fig. S9 AFM image (top) and the height profile (bottom) of the surface of the boundary area scratched PVP film.

Caution) PVP was distorted when scratching because it was very soft.

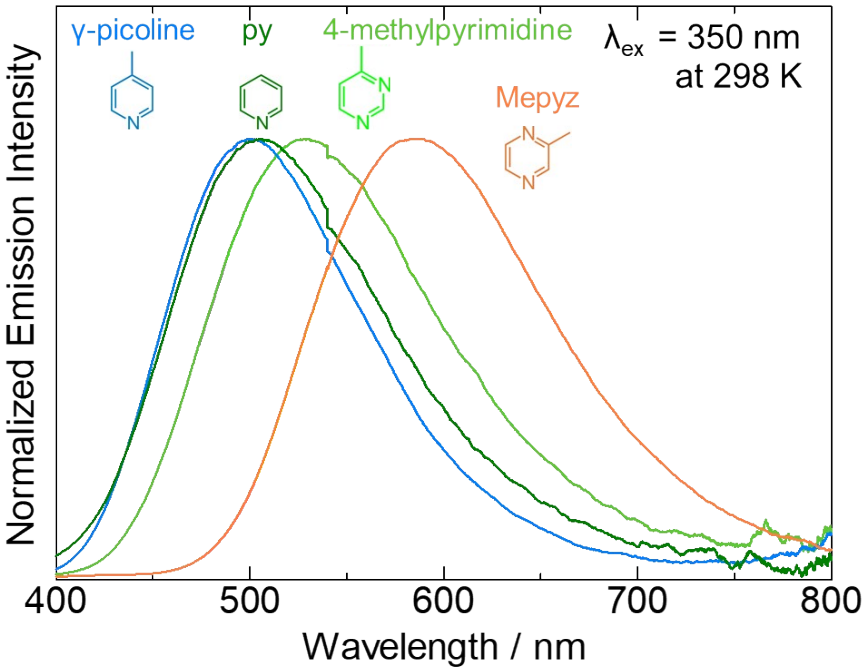


Fig. S10 Emission spectra when **Cu-x@PVP** was exposed to vapour of different N-heteroaromatic compounds: blue, 4-methyl pyridine (blue), pyridine (dark green), 4-methylpyrimidine (light green), and 2-methylpyradine (orange).

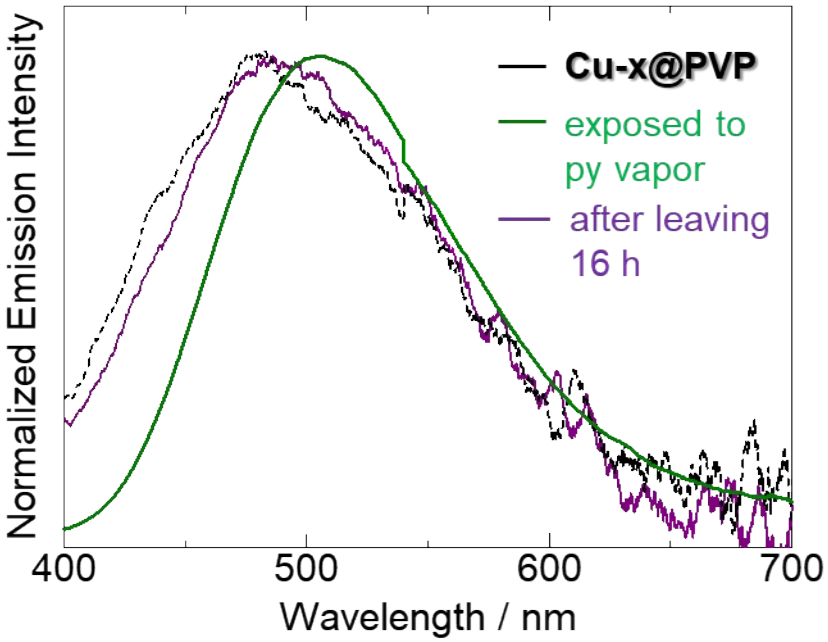


Fig. S11 Emission spectra of **Cu-x@PVP** after py vapor exposure and the film after the subsequent drying (λ_{ex} = 350 nm, at 298 K).

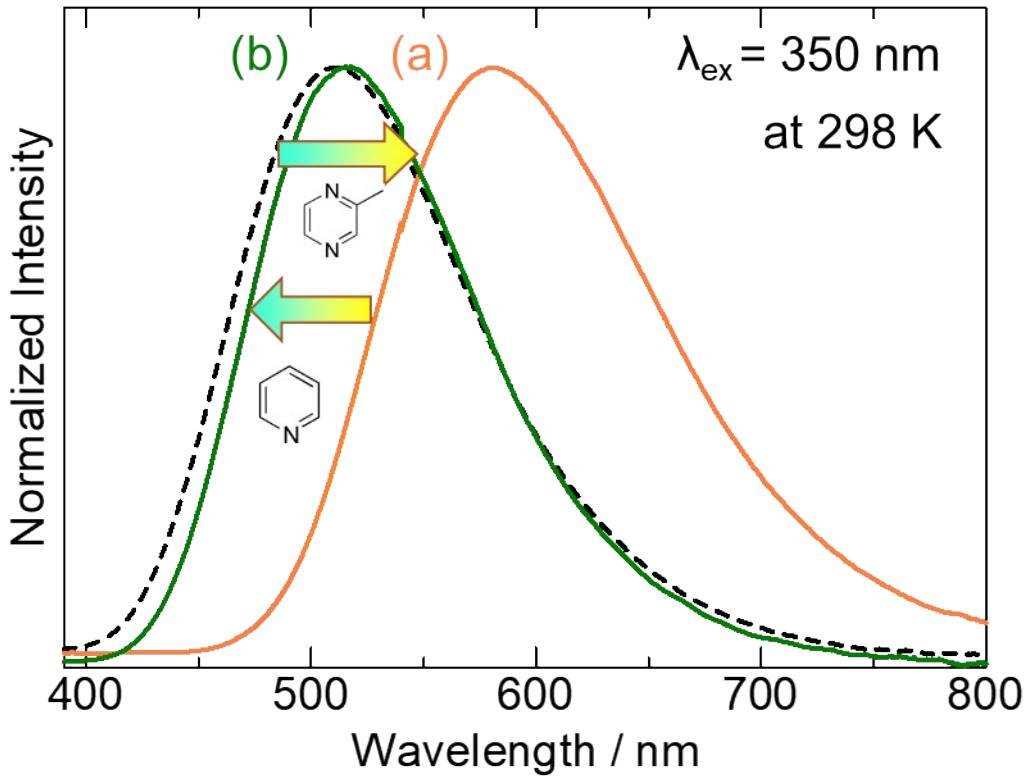


Fig. S12 Emission spectra of **Cu-x-py@PVP** after Mepyz vapor exposure and the film after the subsequent py vapor exposure (λ_{ex} = 350 nm, at 298 K). Black broken line shows **Cu-x-py@PVP** before Mepyz vapor exposure.

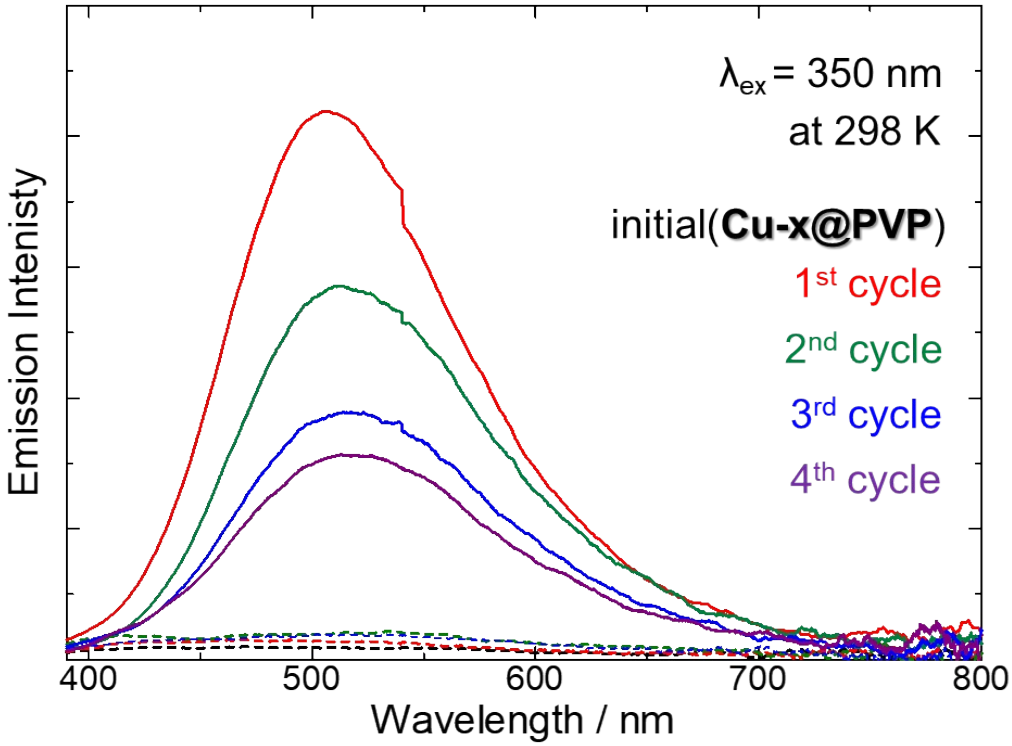


Fig. S13 Emission spectra of **Cu-x@PVP** after repeated py vapor exposure and the film after repeated drying.

Black broken line shows **Cu-x@PVP** before py vapor exposure. All measurements were conducted using the same sample. Red, green, blue and purple lines show **Cu-x@PVP** after first, second, third and fourth py vapor exposure, respectively. Red, green and blue lines show **Cu-x@PVP** after first, second and third py vapor exposure, respectively.

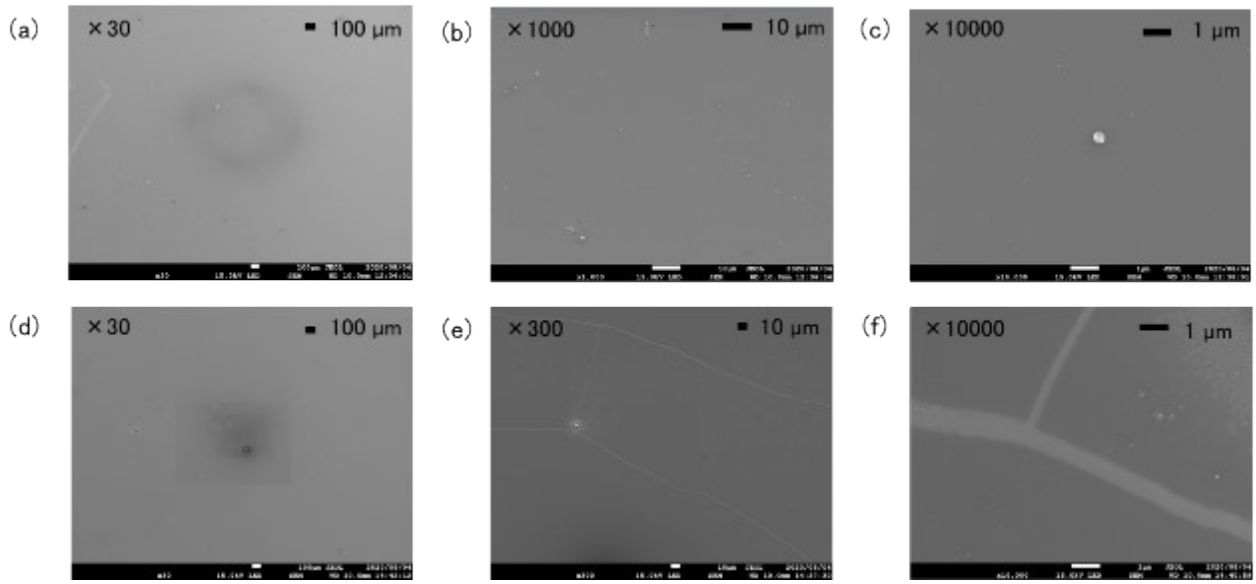


Fig. S14 Surface SEM images of (a)–(c) **Cu-x@PVP** and (d)–(f) **Cu-x-py@PVP**.

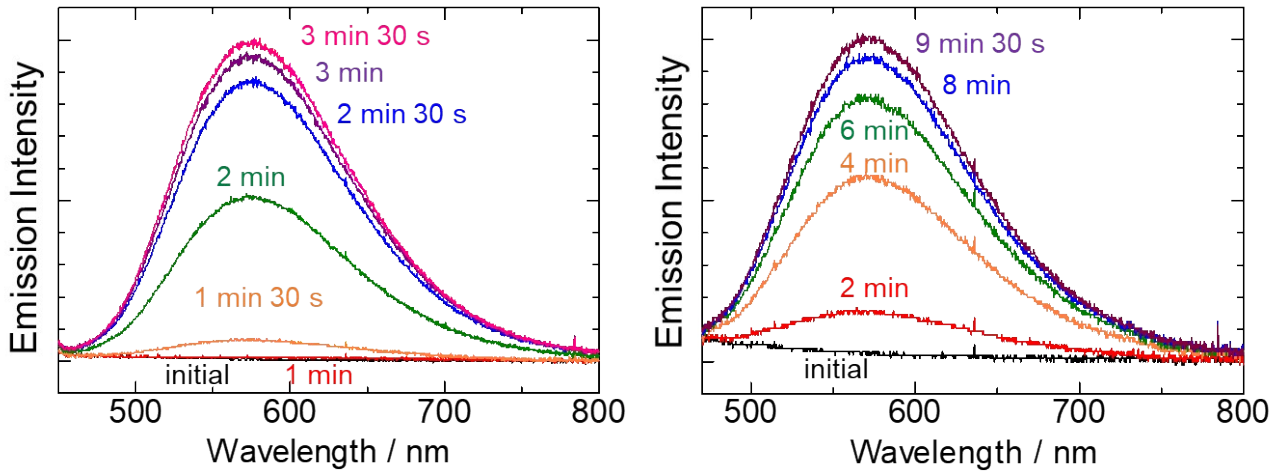


Fig. S15 *In-situ* emission spectral changes of (a) **Cu-x@PVP** and (b) **Cu-x** powder on Mepyz vapour exposure (λ_{ex} = 350−385 nm, at 298 K).

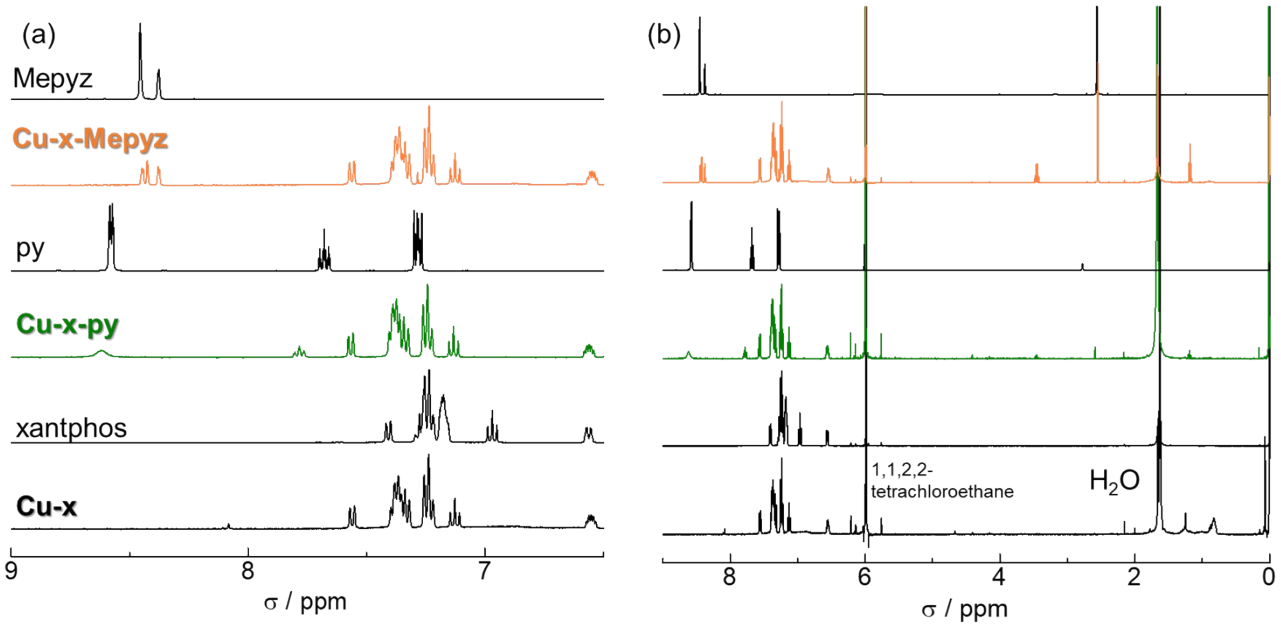


Fig. S16 ^{1}H NMR spectra in of **Cu-x, Cu-x-py,** and **Cu-x-Mepyz**: (a) aromatic region and (b) whole range (at 293 K, 400 MHz, in 1,1,2,2-Tetrachloroethane-d_2). Those of the ligands Mepyz, py, and xantphos are also shown.

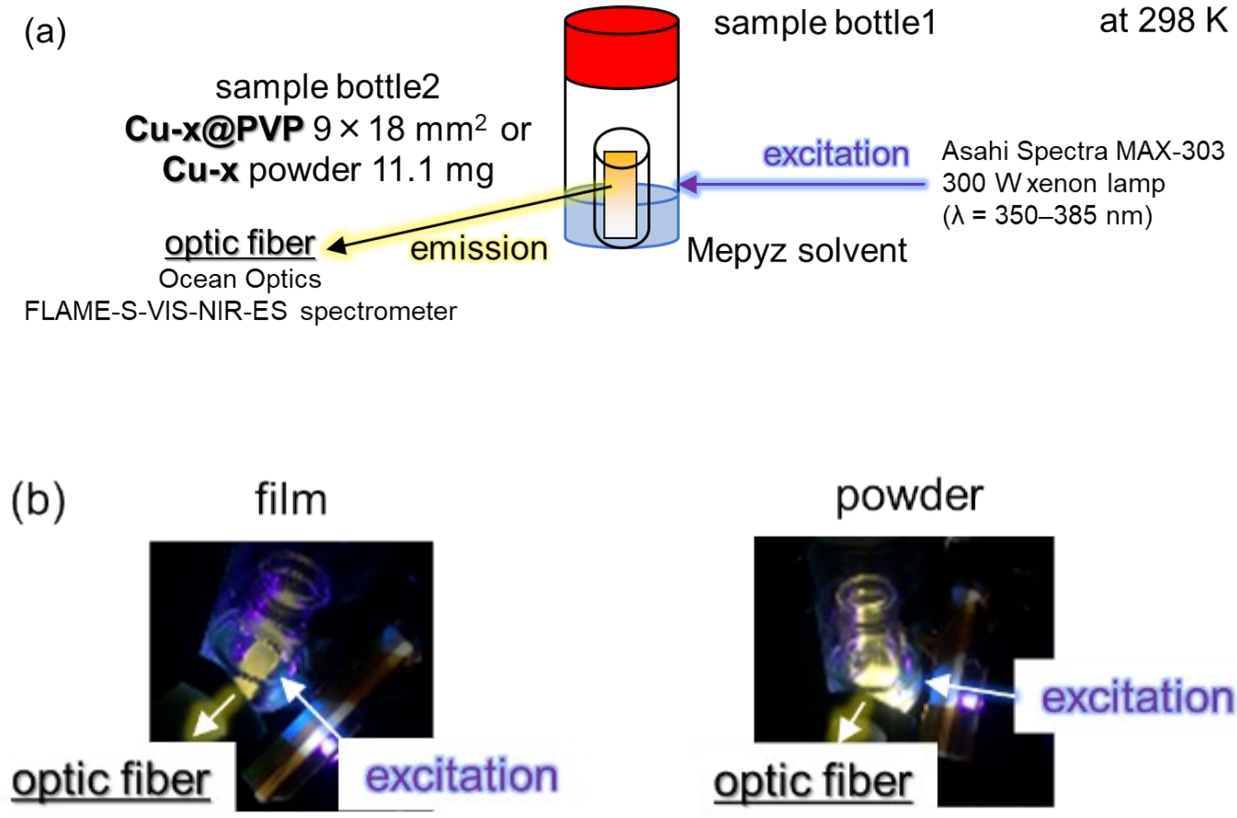


Fig. S17 (a)Schematic images of the experimental setup for *in-situ* emission spectral measurement under vapour exposure and (b) the photos of samples after *in-situ* emission spectral measurement under UV light.

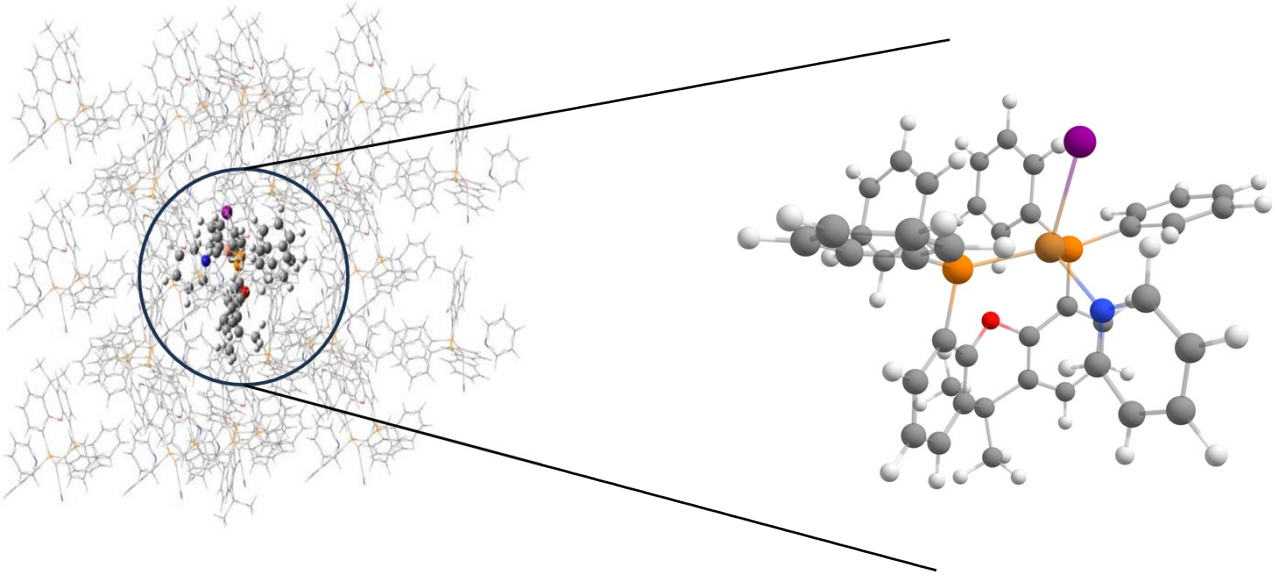


Fig. S18 Cluster model of **Cu-x-py** system. The ONIOM high-layer is shown in "ball and stick", and the ONIOM low-layer is shown in "wireframe".

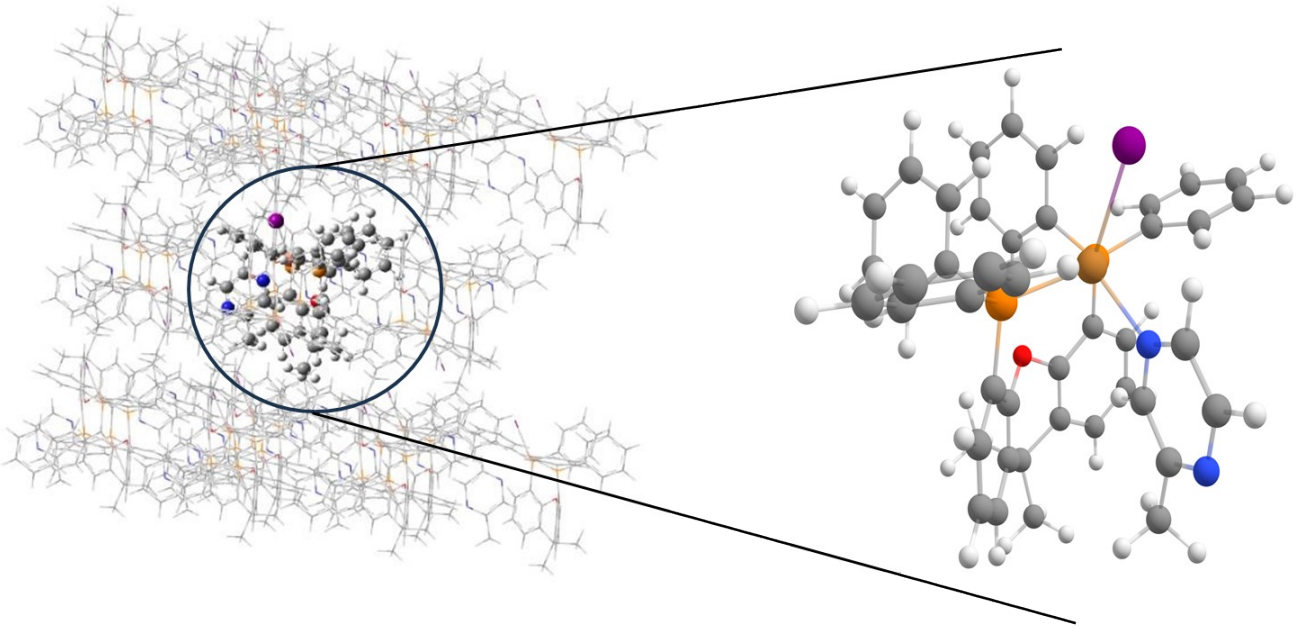


Fig. S19 Cluster model of **Cu-x-Mepyz**. The ONIOM high-layer is shown in "ball and stick", and the ONIOM low-layer is shown in "wireframe".

Table S1. Crystal parameters and refinement data.

Complex	**Cu-x-py**·1.5H_2O ·0.25py	**Cu-x-Mepyz**
T / K	150	150
Formula	$C_{44}H_{37}CuINOP_2$, 1.5(H_2O),0.25(C_5H_5N)	$C_{44}H_{38}CuIN_2OP_2$
Formula weight	894.98	863.20
Crystal system	*triclinic*	*monoclinic*
Space group	*P*-1	$P2_1/c$
a / Å	12.0341(1)	10.0650(1)
b / Å	17.0326(1)	19.0428(2)
c / Å	21.4201(3)	20.0881(2)
α / °	100.472(1)	90
β / °	104.670(1)	93.390(1)
γ / °	90.043(1)	90
V / Å ^{3}	4171.59(8)	3843.46(7)
Z	4	4
D_{cal} / g cm^{-3}	1.425	1.492
Reflections collected	27386	29244
Unique reflections	24775	14554
R_{int}	n/a	0.0256
GOF	1.034	1.065
R_1 ($I > 2\sigma(I)$) [a]	0.0596	0.0570
wR_2 [b]	0.1767	0.1685

[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 the X-ray structures and the optimized ground state structures.

	Cu-x[a]	**Cu-x-py**·1.5H_2O ·0.25py	**Cu-py (DFT)**	**Cu-x Mepyz**	**Cu-x Mepyz (DFT)**
Cu1-I1	2.513(2)	2.626(1), 2.618(1)	2.62	2.565(1)	2.62
Cu1-P1	2.247(3)	2.262(1), 2.262(1)	2.29	2.261(1)	2.30
Cu1-P2	2.259(2)	2.2624(2), 2.269(2)	2.28	2.258(1)	2.30
Cu1…O1	2.83(1)	3.170(3), 3.179(3)	3.26	3.215(3)	3.28
Cu1-N1	-	2.087(5), 2.085(5)	2.15	2.273(4)	2.18
I1-Cu1-P1	116.8(1)	106.80(5), 105.37(5)	110.0	114.30(4)	112.2
I1-Cu1-P2	120.3(1)	111.08(5), 110.34(5)	112.0	115.65(4)	117.8
I1-Cu1-N1	-	106.6(1), 106.2(1)	107.7	103.4(1)	104.3
P1-Cu1-P2	118.7(1)	115.68(6), 116.80(6)	114.8	117.17(5)	114.4

a) J. Huang, J. Chan, Y. Chen, C. J. Borths, K. D. Baucom, R. D. Larsen and M. M. Faul, *J. Am. Chem. Soc*. **2010**, *132*, 3674–3675.

Remarks: Reflecting the three-coordination structure, Cu1-I1 bond length of **Cu-x** was more than 0.05 Å shorter than that of other two complexes. In addition, in **Cu-x**, the O atom in the xantphos ligand is close to the Cu ion at a distance (Cu1⋯O1) of 2.83 (1) Å, which is about 0.4 Å shorter than the other two complexes. On the other hand, there is a marked difference in the Cu1-N1 bond between **Cu-x-py** and **Cu-x-Mepyz**, The very long distance in **Cu-x-Mepyz** would be due to the steric hindrance of the methyl group of the Mepyz ligand. In general, key structural parameters of the optimized ground state structures are in agreement with the X-ray structures.

Table S3. **Cartesian coordinates of the optimized structures (only ONIOM high-layer)**

Cu-x-py

S_0

I	0.35747200	3.16261200	-2.78635800
Cu	-0.28282100	2.07343900	-0.49373300
P	-1.15327800	-0.01276400	-0.83348200
P	1.43621800	2.16293000	1.00468200
C	-2.11920800	-0.63641700	0.59995800
O	-0.21768300	-0.13609600	1.90137300
N	-1.87881800	3.24027300	0.36297700
C	0.05782200	-1.35039900	-1.11691700
C	2.87186300	1.14578000	0.50788000
C	-1.52626300	-0.55372400	1.85935400
C	-0.20197800	-2.67504000	-0.76547000
H	-1.14053000	-2.93529600	-0.28818600
C	0.13445200	0.64042400	2.97662700
C	-2.36324300	-0.18241000	-2.19539700
C	-3.52890000	-1.24129300	2.93665600
H	-4.08579100	-1.46695400	3.83558400
C	1.37920700	2.47932700	3.84012200
H	2.04783900	3.31934000	3.70615400
C	2.19465000	3.81673400	1.21321400
C	1.27111000	-1.02200200	-1.72068300
H	1.47922500	0.01120100	-1.97561000
C	1.02450800	1.69349000	2.74291600
C	-3.44326300	-1.06519000	0.53585900
H	-3.93354600	-1.14425000	-0.42720300
C	1.93250100	-3.33350400	-1.65834200
H	2.64521900	-4.11570600	-1.88534600
C	-2.19991100	-0.84644900	3.04033000
C	-0.43432700	0.37865000	4.22303800
C	2.20613800	-2.01375000	-1.99144000
H	3.15064700	-1.74962200	-2.45151000
C	0.84163400	2.23383900	5.09327500
H	1.11159300	2.87410800	5.92201200
C	-1.40890900	-0.79237100	4.34277900

C	-4.14296100	-1.36296200	1.69759500
H	-5.17393000	-1.69022300	1.63463200
C	3.48131400	3.99136600	1.72725300
H	4.07626100	3.12564200	1.99950600
C	-2.46145700	-1.31526400	-3.00030500
H	-1.75995200	-2.13224200	-2.87762600
C	-0.06657000	1.20217200	5.28078500
H	-0.49900100	1.04512200	6.26019100
C	-4.24814700	0.78953600	-3.35398700
H	-4.93143900	1.61792100	-3.50301500
C	4.00226300	5.26633300	1.88665800
H	5.00040800	5.38786100	2.28743300
C	-3.24463200	0.88218900	-2.39976700
H	-3.13637900	1.78755900	-1.81186500
C	0.73504800	-3.66083700	-1.03498200
H	0.53036600	-4.68717500	-0.76190700
C	3.26999000	-0.00306100	1.18202100
H	2.72162400	-0.32826900	2.05679100
C	3.54677100	1.53539000	-0.65438600
H	3.21552700	2.40695300	-1.21060300
C	3.24691400	6.37775100	1.52589100
H	3.65833500	7.37365100	1.63274000
C	1.44703200	4.93413800	0.84560100
H	0.46374800	4.79865100	0.41039200
C	5.05733600	-0.31985500	-0.39649200
H	5.93097300	-0.86378700	-0.73047200
C	-0.60416800	-2.10448000	4.44233700
H	0.07378000	-2.07801700	5.29859000
H	-0.02342900	-2.24909800	3.53134700
H	-1.28021800	-2.95638000	4.55487100
C	-2.48553300	2.86873500	1.49311500
H	-2.01648800	2.06798200	2.05267500
C	-3.66002900	3.44926000	1.93994700
H	-4.11814700	3.09362800	2.85243600
C	-4.36014100	-0.35841900	-4.12930100
H	-5.14324600	-0.44553600	-4.87076800
C	-2.40660100	4.24324600	-0.34392700
H	-1.86182000	4.50100500	-1.24664200

C	4.36546000	-0.73331200	0.73345200
H	4.67881200	-1.62107500	1.27169200
C	-2.30929300	-0.66806800	5.57414700
H	-2.98686600	-1.52161000	5.64477200
H	-2.90434900	0.24889500	5.55675000
H	-1.70892000	-0.67660500	6.48622200
C	-4.22177100	4.46946600	1.18656100
H	-5.15405300	4.92919300	1.48250300
C	-3.45486700	-1.39686200	-3.96762400
H	-3.52292200	-2.27235400	-4.59992400
C	4.63697400	0.80440200	-1.09985400
H	5.16574600	1.11974600	-1.99238500
C	1.97149500	6.21151100	1.00509000
H	1.38883900	7.07506200	0.70557900
C	-3.57407900	4.88787500	0.03465900
H	-3.97292500	5.69238900	-0.56878700

S_1

I	0.67178100	2.87750600	-2.75906800
Cu	-0.37642800	2.24425800	-0.52254900
P	-1.22677900	-0.00147700	-0.86177700
P	1.39072400	2.31677300	1.03350000
C	-2.16457300	-0.60889700	0.58634600
O	-0.28895900	0.02727700	1.85745700
N	-1.77275800	3.16286400	0.43424800
C	0.00874700	-1.32466900	-1.12694500
C	2.79405200	1.23214000	0.58756100
C	-1.56519800	-0.48667000	1.83682600
C	-0.25821900	-2.64961200	-0.77589900
H	-1.20541600	-2.90930100	-0.31606800
C	0.05462300	0.77541700	2.95426400
C	-2.43537100	-0.16272500	-2.21323800
C	-3.51456500	-1.28114200	2.92909500
H	-4.05348900	-1.52909400	3.83261300
C	1.28758600	2.61625000	3.84732100
H	1.93956900	3.47095500	3.71953200
C	2.12774900	3.97127500	1.20439000
C	1.23813200	-1.00251200	-1.70111000

H	1.46150300	0.02615300	-1.95631600
C	0.91825700	1.85185000	2.74204400
C	-3.46512900	-1.10168400	0.52965800
H	-3.95969000	-1.20183100	-0.42907800
C	1.89565600	-3.31447200	-1.62021800
H	2.61211200	-4.09845100	-1.82980500
C	-2.20560200	-0.82317600	3.02285700
C	-0.47419300	0.46035800	4.20414000
C	2.17736000	-1.99621600	-1.94980800
H	3.13039900	-1.73327800	-2.39298000
C	0.78962400	2.31470500	5.10388800
H	1.06752300	2.92759100	5.94984000
C	-1.40904600	-0.74205100	4.32003800
C	-4.13771000	-1.42965700	1.69802300
H	-5.15551200	-1.79696400	1.64846500
C	3.44198400	4.15300900	1.63855400
H	4.05789200	3.29389300	1.88119700
C	-2.50354100	-1.27563800	-3.04825300
H	-1.77893300	-2.07593400	-2.95219000
C	-0.09213800	1.25786000	5.27615900
H	-0.49502700	1.05958000	6.26042500
C	-4.35639800	0.78686500	-3.31906200
H	-5.07080500	1.59404600	-3.43087100
C	3.96232000	5.43287400	1.75282000
H	4.98306900	5.56497100	2.08555200
C	-3.35172200	0.88199600	-2.36622800
H	-3.28365600	1.76209200	-1.73287000
C	0.68403600	-3.63674900	-1.02185400
H	0.47310000	-4.66223500	-0.75073700
C	3.08072100	0.06485300	1.29026800
H	2.46836300	-0.22034300	2.13578300
C	3.56504300	1.57036500	-0.52887000
H	3.33625100	2.46302800	-1.10029500
C	3.17831000	6.53514900	1.43053300
H	3.59420400	7.53293900	1.49496600
C	1.33843100	5.07928000	0.89553700
H	0.31395900	4.94502000	0.56660300
C	4.93870200	-0.37374900	-0.17323500

H	5.79827000	-0.97275200	-0.44549200
C	-0.55437000	-2.02300800	4.40866600
H	0.10648100	-1.98643300	5.27780700
H	0.04935500	-2.12605500	3.50600100
H	-1.19694700	-2.90371300	4.49209400
C	-2.48291600	2.79375700	1.56170500
H	-2.09582000	1.96063700	2.12709300
C	-3.61550600	3.43499600	1.95856200
H	-4.11895500	3.07760600	2.84836100
C	-4.43652600	-0.33911900	-4.13031400
H	-5.22224000	-0.42712800	-4.86786000
C	-2.20991700	4.30939800	-0.23381400
H	-1.61669900	4.63085500	-1.07874600
C	4.15546600	-0.73253200	0.91470100
H	4.38201900	-1.63018100	1.47876300
C	-2.30760200	-0.65370100	5.55639700
H	-2.95312000	-1.53158700	5.62788100
H	-2.93461900	0.24125700	5.54171500
H	-1.70459300	-0.64399500	6.46665200
C	-4.11248900	4.54274800	1.23067500
H	-5.02998400	5.03814500	1.50102800
C	-3.50354500	-1.35819600	-4.00773700
H	-3.55739300	-2.21983100	-4.66035500
C	4.63071900	0.76760400	-0.90629300
H	5.23158700	1.04500800	-1.76515100
C	1.86735900	6.35859300	1.00907900
H	1.25407000	7.21511900	0.75645800
C	-3.34556500	4.97620100	0.14181900
H	-3.63923100	5.85265700	-0.42475700

T_1

I	0.34686300	3.07950800	-2.82325200
Cu	-0.27723400	2.05508300	-0.50933100
P	-1.17005400	-0.04130000	-0.85825900
P	1.45597800	2.14492700	0.99158700
C	-2.11961800	-0.62770600	0.52263500
O	-0.20932500	-0.12040800	1.89550700
N	-1.87916300	3.20097400	0.33102500

C	0.08352500	-1.34471600	-1.13961400
C	2.89730300	1.14382700	0.48044100
C	-1.50794300	-0.55520000	1.88901700
C	-0.17797500	-2.66448600	-0.76931100
H	-1.11982800	-2.90732900	-0.28819200
C	0.16944100	0.63299700	2.97412300
C	-2.35013600	-0.17862400	-2.24278500
C	-3.55221400	-1.19776100	2.95096700
H	-4.12067100	-1.40863600	3.84255100
C	1.43703000	2.46225600	3.82695200
H	2.10675500	3.30012500	3.68733200
C	2.19776700	3.80846700	1.18853300
C	1.29608000	-1.01892300	-1.74347700
H	1.50333200	0.01224800	-2.00574200
C	1.06643500	1.67866200	2.73443200
C	-3.53221800	-0.99275200	0.49008300
H	-4.02790700	-1.06175500	-0.47034900
C	1.95169700	-3.33239400	-1.66170300
H	2.66079500	-4.11810200	-1.88714000
C	-2.18002100	-0.81760200	3.04246300
C	-0.39561800	0.37627900	4.22335500
C	2.22867400	-2.01529600	-2.00504400
H	3.17385000	-1.75839900	-2.46777600
C	0.90757100	2.21921200	5.08429500
H	1.18802500	2.85729900	5.91094000
C	-1.39718400	-0.77166400	4.35110000
C	-4.19831700	-1.28536700	1.62980400
H	-5.23353000	-1.60260000	1.58149000
C	3.48553900	3.99270300	1.69671700
H	4.08860100	3.13118700	1.96391600
C	-2.44643200	-1.31313600	-3.04515800
H	-1.74512800	-2.12996900	-2.92031600
C	-0.00877300	1.19631400	5.27745600
H	-0.43811000	1.04503000	6.25888700
C	-4.24045500	0.78779700	-3.39294800
H	-4.92759500	1.61338000	-3.53938200
C	3.99572900	5.27140600	1.86074600
H	4.99413100	5.40007900	2.25861200

C	-3.23296000	0.88483200	-2.44334600
H	-3.12641000	1.78889400	-1.85344800
C	0.75624400	-3.65423400	-1.03160100
H	0.55060300	-4.67807900	-0.74968100
C	3.31045200	-0.00259500	1.14982900
H	2.77396300	-0.33260600	2.03026400
C	3.55934100	1.54175600	-0.68626900
H	3.21801500	2.41285000	-1.23682300
C	3.22876700	6.37805200	1.51043600
H	3.63210400	7.37684700	1.62226000
C	1.43842300	4.92137700	0.83187100
H	0.45212600	4.78136800	0.40528800
C	5.08341100	-0.30426800	-0.44781500
H	5.95567300	-0.84253800	-0.79371200
C	-0.63065800	-2.10263000	4.48368700
H	0.03381300	-2.08638600	5.35118600
H	-0.04107600	-2.27369000	3.58334500
H	-1.33217600	-2.93416800	4.59406400
C	-2.51630100	2.80965300	1.43766900
H	-2.10883800	1.94766700	1.95416700
C	-3.65074400	3.44513900	1.91206000
H	-4.13372700	3.07775500	2.80691700
C	-4.35566500	-0.36392400	-4.16204900
H	-5.14634800	-0.45785500	-4.89442600
C	-2.33817400	4.26827000	-0.32835800
H	-1.77466600	4.53772100	-1.21620900
C	4.40630400	-0.72435100	0.68861800
H	4.73113700	-1.61098900	1.22181200
C	-2.30593500	-0.60033000	5.57207800
H	-3.00926300	-1.43223400	5.64586800
H	-2.87360500	0.33312500	5.53407900
H	-1.71635600	-0.61312500	6.49143300
C	-4.14102500	4.53513400	1.20849600
H	-5.04196900	5.03967300	1.52545000
C	-3.44665600	-1.39981900	-4.00431300
H	-3.52095100	-2.27943700	-4.62963100
C	4.65021100	0.81953500	-1.14369500
H	5.16921700	1.14063800	-2.03978400

C	1.95212600	6.20274500	0.99549300
H	1.35913900	7.06272500	0.70617100
C	-3.46491600	4.96517300	0.07746100
H	-3.80980800	5.81924000	-0.48981000

Cu-x-Mepyz

S_0

I	0.66241800	4.15424900	-0.92526800
Cu	0.95251100	1.70690600	-0.04981900
P	-0.94701400	0.92085200	0.97241200
P	2.90815800	1.18280200	1.04812500
O	1.14462400	-1.05825900	1.70404100
C	-2.53438700	1.44383800	0.21892400
C	0.02346800	-1.70562400	1.24115300
C	4.43985100	1.98753700	0.44379200
C	-1.09317100	-0.91863800	0.94412200
C	3.34806500	-0.60423400	0.97888200
C	0.06703600	-3.08072400	1.02104800
C	5.63253700	1.98912500	1.17119000
H	5.66546000	1.52526300	2.15006300
C	2.35234900	-1.54335200	1.25889600
C	-2.21292000	-1.57091500	0.43051100
H	-3.08333900	-0.98674900	0.16511700
C	2.51807700	-2.91060300	1.05876500
C	2.90052600	1.53550400	2.84349500
C	-1.07236400	-3.68749200	0.50192700
H	-1.07675000	-4.75250700	0.31018200
C	-1.17663800	1.40972000	2.71851500
C	4.57700500	-1.08602200	0.53261000
H	5.37067500	-0.39077900	0.29179400
C	3.43893900	0.67045400	3.79378500
H	3.87428600	-0.27234300	3.48365400
C	-3.72129800	1.51437000	0.94988900
H	-3.71654800	1.27379000	2.00612200
C	3.76391400	-3.34947100	0.62327700
H	3.93617800	-4.40758800	0.47930500

C	6.76973800	2.58886300	0.64953600
H	7.68872000	2.59176300	1.22311500
C	-1.48982500	0.50797900	3.72894700
H	-1.57640600	-0.54422100	3.49449100
C	2.32061500	2.73406100	3.25903900
H	1.86921200	3.39332200	2.52483000
C	-2.54369000	1.77710700	-1.13522000
H	-1.61639100	1.76426800	-1.69591200
C	2.31341900	3.07728700	4.60358600
H	1.86555900	4.01310700	4.91499000
C	-2.20553800	-2.94233100	0.21624700
H	-3.08041400	-3.43466500	-0.18900200
C	-1.06310600	2.76915800	3.02073800
H	-0.80610400	3.47671900	2.23730800
C	4.78793000	-2.44847300	0.37280800
H	5.75466100	-2.80547600	0.04132700
C	1.34601100	-3.83256800	1.37857500
C	-1.27836600	3.21130500	4.31797300
H	-1.19402200	4.26751900	4.54491400
C	-1.69617400	0.95260400	5.02905300
H	-1.94213400	0.23630900	5.80417000
C	-1.59408100	2.30507000	5.32515400
H	-1.76010300	2.65448800	6.33803700
C	3.41162800	1.00717700	5.14058700
H	3.82322900	0.31959500	5.87053400
C	2.86073100	2.21617100	5.54635000
H	2.85290300	2.48381400	6.59650100
C	-4.90231100	1.90189100	0.33258100
H	-5.81790500	1.95682000	0.90928500
C	1.43712000	-5.17361800	0.65653200
H	0.61141200	-5.81692500	0.96547800
H	2.35337000	-5.69674300	0.92922500
H	1.41100900	-5.06357600	-0.43013400
C	4.39975300	2.60754600	-0.80414900
H	3.46525100	2.64820100	-1.35216500
C	6.72347200	3.20045900	-0.59982600
H	7.60708400	3.68253600	-1.00078400
C	1.35170600	-4.07229500	2.89620200

H	1.33795800	-3.10214300	3.38197300
H	2.25453600	-4.60614100	3.20208600
H	0.47344600	-4.64062000	3.20963800
C	-4.90535800	2.22537900	-1.01967700
H	-5.82301800	2.54356000	-1.49840800
C	-3.72747100	2.16197800	-1.75257400
H	-3.72423600	2.43357200	-2.80150900
C	5.53956200	3.21173000	-1.32359000
H	5.49279900	3.70615200	-2.28669200
C	1.73157000	-3.08527800	-2.76423600
H	2.55500900	-3.29468600	-2.07544700
H	1.96222800	-3.50702000	-3.74200700
H	0.83449800	-3.57024900	-2.36739600
C	1.37354100	0.25965300	-4.18738500
H	1.41029700	0.69644400	-5.17965600
C	1.12064800	1.04558600	-3.07747200
H	0.97237000	2.11904800	-3.13034000
N	1.05807500	0.49495700	-1.86402900
C	1.22870800	-0.81865300	-1.78425800
H	1.14542600	-1.27138000	-0.81072800
C	1.51285800	-1.60615500	-2.89533500
N	1.59160500	-1.04957700	-4.09632500

S_1

I	0.47740300	4.01924400	-0.50268100
Cu	0.86570200	1.51463900	-0.25317400
P	-1.01613600	0.78526700	0.89532700
P	2.94579600	1.09983700	0.98552900
O	1.15103200	-1.09634200	1.63014200
C	-2.57057600	1.27391500	0.08863600
C	0.03147600	-1.78819700	1.24593100
C	4.45859500	1.90749900	0.36123300
C	-1.10383600	-1.03964200	0.93116200
C	3.36868900	-0.67965000	0.93781500
C	0.08065200	-3.17119600	1.09643900
C	5.62433200	2.01145300	1.12285600
H	5.63854900	1.63490600	2.13888100
C	2.36410500	-1.60504800	1.21565300

C	-2.22731800	-1.71885600	0.46758000
H	-3.10163300	-1.15037400	0.18575800
C	2.53410900	-2.97629700	1.06359400
C	2.91538500	1.49078800	2.77318000
C	-1.06213100	-3.81012800	0.62872200
H	-1.04986700	-4.88089600	0.47959700
C	-1.19031900	1.35067300	2.62299600
C	4.60635300	-1.16628300	0.52664100
H	5.40383200	-0.47482200	0.28743500
C	3.44227100	0.63802200	3.74185600
H	3.87910400	-0.30892900	3.44800400
C	-3.71831400	1.59303700	0.81307900
H	-3.69829700	1.58473800	1.89647600
C	3.78357400	-3.42200900	0.64981500
H	3.95470000	-4.48188400	0.52430300
C	6.75924800	2.60103700	0.58531900
H	7.65950000	2.67794200	1.18283700
C	-1.48236500	0.45566900	3.64825700
H	-1.56192900	-0.59818400	3.42512600
C	2.33398300	2.69611500	3.16713800
H	1.89415700	3.34965800	2.42143500
C	-2.59500300	1.29277800	-1.30679900
H	-1.69952900	1.04525000	-1.86739200
C	2.31218300	3.05786500	4.50694900
H	1.86416200	3.99981700	4.80006400
C	-2.21072900	-3.09704900	0.32338600
H	-3.08538400	-3.61685600	-0.04639100
C	-1.08464800	2.71300800	2.91131300
H	-0.84575400	3.41864500	2.12324000
C	4.81449600	-2.53025800	0.39525900
H	5.78352800	-2.89594200	0.08182900
C	1.37671500	-3.89693000	1.43669200
C	-1.28178100	3.16474300	4.20833500
H	-1.19721300	4.22345000	4.42370500
C	-1.67729000	0.91108700	4.94551500
H	-1.91046200	0.20149600	5.73065600
C	-1.57827900	2.26681100	5.22771600
H	-1.73132800	2.62419200	6.23977800

C	3.40382600	0.99502500	5.08328000
H	3.81079600	0.31974800	5.82728100
C	2.84887400	2.20949300	5.46721200
H	2.83114700	2.49125300	6.51368400
C	-4.88626200	1.93321800	0.14316000
H	-5.77574500	2.18487300	0.70827900
C	1.45329600	-5.25884900	0.75611300
H	0.65649700	-5.90417200	1.13036000
H	2.39028400	-5.75682200	0.99721600
H	1.37103900	-5.18879700	-0.33008000
C	4.44086900	2.40534000	-0.94115100
H	3.53827500	2.32977900	-1.53812400
C	6.73426600	3.09994100	-0.71302800
H	7.61472600	3.57330800	-1.13021100
C	1.43476900	-4.08792500	2.95974000
H	1.47994400	-3.10090800	3.40869100
H	2.33250100	-4.63994400	3.24566400
H	0.55343900	-4.61656700	3.33028600
C	-4.90774900	1.95318800	-1.24563300
H	-5.81070600	2.23437300	-1.77061500
C	-3.76666700	1.62745700	-1.96854100
H	-3.78488600	1.64513600	-3.04991400
C	5.57752600	3.00202200	-1.47388900
H	5.55474300	3.39683000	-2.48172900
C	1.59790300	-3.28347600	-2.87521800
H	1.33056800	-3.69754200	-1.90076300
H	2.62257800	-3.57923900	-3.11490000
H	0.94802400	-3.72132400	-3.63793200
C	1.45590900	0.14921100	-4.07163000
H	1.54757000	0.65911100	-5.02693100
C	1.09407600	0.87559100	-2.97146900
H	0.91817400	1.94106100	-3.02878800
N	0.95335700	0.26252900	-1.73793600
C	1.09003700	-1.10934700	-1.76560400
H	0.88470800	-1.64865300	-0.86126600
C	1.46221600	-1.78693800	-2.88979600
N	1.70758400	-1.17281300	-4.06998700

T_1

I	0.53409900	4.05572700	-0.60002300
Cu	0.86819200	1.54001000	-0.29083000
P	-1.00908100	0.76630800	0.87538100
P	2.94134500	1.08781200	0.93260900
O	1.15670000	-1.10518000	1.61439100
C	-2.57302400	1.25305100	0.08228200
C	0.03367900	-1.80239700	1.25005600
C	4.45809600	1.90242300	0.32740600
C	-1.10499800	-1.05731700	0.93853900
C	3.36550700	-0.68980500	0.89371900
C	0.08503400	-3.18574400	1.10674600
C	5.61834200	1.99767100	1.09914100
H	5.62783600	1.60556200	2.10956300
C	2.36445900	-1.61436500	1.18734800
C	-2.22911200	-1.74087200	0.48419900
H	-3.10461600	-1.17419100	0.20257300
C	2.53710400	-2.98617400	1.04648000
C	2.89712600	1.48311300	2.71957900
C	-1.05954600	-3.82944500	0.64923900
H	-1.04534400	-4.90087200	0.50570800
C	-1.17553700	1.35277500	2.59725000
C	4.60269200	-1.17644800	0.48190300
H	5.39730600	-0.48492700	0.23330700
C	3.42554900	0.63668200	3.69346000
H	3.86418100	-0.31158700	3.40611100
C	-3.71778700	1.56339400	0.81575900
H	-3.69248200	1.54186200	1.89887700
C	3.78634400	-3.43267300	0.63259800
H	3.96000800	-4.49348800	0.51975600
C	6.75414900	2.60082900	0.57908600
H	7.64989000	2.67252600	1.18409600
C	-1.46554800	0.47716000	3.63972500
H	-1.54863900	-0.58109100	3.43775200
C	2.31661800	2.69105500	3.10542100
H	1.87977200	3.34088900	2.35470700
C	-2.60498800	1.29143600	-1.31233700
H	-1.71145400	1.05332400	-1.87983700

C	2.29347800	3.06066100	4.44318800
H	1.84460100	4.00412300	4.72995300
C	-2.21099300	-3.11997700	0.34626500
H	-3.08687200	-3.64295000	-0.01633000
C	-1.06682900	2.72022800	2.85932200
H	-0.83018700	3.41025900	2.05620000
C	4.81430600	-2.54117100	0.36538800
H	5.78423400	-2.90705500	0.05525600
C	1.38579400	-3.90636600	1.43827800
C	-1.25783300	3.19611800	4.14868300
H	-1.16937700	4.25821500	4.34449300
C	-1.65543100	0.95736400	4.92898100
H	-1.88795300	0.26329700	5.72810000
C	-1.55301100	2.31798300	5.18551100
H	-1.70262300	2.69445500	6.19120700
C	3.38747700	1.00268200	5.03250200
H	3.79633500	0.33396400	5.78154300
C	2.83018200	2.21864500	5.40877800
H	2.81122100	2.50632100	6.45371600
C	-4.88837200	1.91400200	0.15626800
H	-5.77468300	2.15980000	0.72899000
C	1.45809300	-5.27080700	0.76283100
H	0.66621100	-5.91626100	1.14699300
H	2.39823900	-5.76601400	0.99624600
H	1.36608700	-5.20414600	-0.32283800
C	4.44653000	2.42358300	-0.96540600
H	3.54594000	2.35952500	-1.56628800
C	6.73535100	3.12271200	-0.71049600
H	7.61621300	3.60812300	-1.11272500
C	1.46099500	-4.08965500	2.96177300
H	1.51791900	-3.10152400	3.40778700
H	2.35895000	-4.64550700	3.23884800
H	0.58165700	-4.61261100	3.34516300
C	-4.91633000	1.95368200	-1.23213300
H	-5.82082500	2.24518300	-1.74868100
C	-3.77924600	1.63643000	-1.96456700
H	-3.80159800	1.67119200	-3.04549800
C	5.58400400	3.03419000	-1.48035300

H	5.56464900	3.44893600	-2.48016600
C	1.58918600	-3.27730500	-2.81910000
H	1.18391400	-3.68556500	-1.89083900
H	2.64065200	-3.56645100	-2.90045200
H	1.06067700	-3.72251000	-3.66578300
C	1.50552700	0.14210400	-4.06002100
H	1.62755300	0.64001900	-5.01766500
C	1.09356000	0.88483900	-2.98709000
H	0.91084300	1.94730000	-3.06394400
N	0.89227500	0.27875800	-1.75781200
C	1.01359700	-1.09503800	-1.76474400
H	0.73853700	-1.62705900	-0.87494500
C	1.44898900	-1.78145600	-2.86302300
N	1.75682400	-1.17813100	-4.03189200

Appendix 1

Evaluation of apparent vapochromic response constant k_{obs}**.**

Given the excess amount of Mepyz, the apparent emission intensity I in the reaction (1) increases depending on the concentration of **Cu-x** following the pseudo-first-order rate low.

$$\textbf{Cu-x} + \text{Mepyz (g)} \rightarrow \textbf{Cu-x-Mepyz} \qquad (1)$$

The apparent reaction rate constant k_{obs} is described as follows:

$$d[\textbf{Cu-x}]/dt = -k_{obs}\,[\textbf{Cu-x}]$$

$$[\textbf{Cu-x}] = [\textbf{Cu-x}]_0 \exp(-k_{obs}t)$$

$$[\textbf{Cu-x-Mepyz}] = [\textbf{Cu-x}]_0 - [\textbf{Cu-x}]$$

$$[\textbf{Cu-x-Mepyz}] = [\textbf{Cu-x}]_0(1 - \exp(-k_{obs}\,(t - t_0)))$$

Assuming the emission intensity I is proportional to the amount of [**Cu-x-Mepyz**] and the intensity of $[\textbf{Cu-x}]_0$ is ignored,

$$I = C\,(1-\exp(-k_{obs}\,(t - t_0))) \qquad (2)$$

Where t_0 is the start time of the ligand addition reaction and C is a coefficient.

$$I - C = -C \exp(-k_{obs}\,(t - t_0))$$

When $t = \infty$, then C converges to 1.

$$I - 1 = -\exp(-k_{obs}\,(t - t_0))$$

$$1 - I = \exp(-k_{obs}\,(t - t_0))$$

$$\ln(I - 1) = -k_{obs}\,(t - t_0) \quad \cdot\cdot\cdot (3)$$

From the emission intensity evolution on vapor exposure shown in **Fig. 10**, k_{obs} and t_0 were determined by the least square fitting based on equation (3). **Cu-x@PVP**: $k_{obs} = 3\times10^{-2}$ s^{-1} (C = 1, t_0 = 95.73 s), **Cu-x** powder: $k_{obs} = 5\times10^{-3}$ s^{-1} (C = 1, t_0 = 93.72 s). The results are shown in **Fig. 10**.