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Reversible luminescent colour changes of mononuclear copper(I) complexes based on ligand exchange reactions by *N*-heteroaromatic vapours<sup>+</sup>

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 $[CuCl(PPh_3)_2(4-Mepy)]$  (PPh<sub>3</sub> = triphenylphosphine, 4-Mepy = 4-methylpyridine), a highly blue-luminescent mononuclear copper(I) complex, shows reversible emission colour change ranging from blue-green to red by vapour exposure to *N*-heteroaromatics such as pyridine, pyrimidine, and 2-methylpyrazine. The remarkable colour changes occur by the ligand exchange reaction between solid and gas. Such ligand exchange reactions would be applicable to various vapours with coordination ability and useful for the sensing of such volatile organic compounds as well as a new convenient methodology for the preparation of luminescent complexes.

## Introduction

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Stimulus-responsive luminescent materials have attracted much attention because they can be potentially applied in naked-eye sensors and memory devices.<sup>1</sup> In most cases, the emission colour changes of these materials are based on hostguest interactions<sup>2</sup> or intermolecular interactions such as hydrogen bonds,<sup>3</sup>  $\pi$ - $\pi$  interactions,<sup>4</sup> or donor-acceptor interactions.<sup>5</sup> From the viewpoint of sensors, it is desirable to show large colour changes in response to external stimuli, both sensitively and selectively. In addition, multipleresponses in recognising various stimuli would be useful in intelligent sensors. Sensor materials that can quickly and easily detect volatile organic compounds (VOCs) should be important environmental monitoring. Platinum(II) and Gold(I) in complexes that exhibit intense luminescence by assembling have been developed for vapor response systems, i.e. vapochromic compounds.<sup>6,7</sup> Luminescent supramolecular systems and porous coordination polymers have also been applied for vapor sensing.<sup>8,9</sup> However, the VOC sensors reproted so far still have limitations on the selective and multiple detection of vapour molecules because of difficulties in the fine control of intermolecular interactions, crystal structures, or pore size of materials. A possible strategy to overcome this issue is the fabrication of sensor arrays that detect a particular vapour was attained by pattern recognition.10

Direct coordination of vapour molecules to the metal sites of transition metal complexes is another promising strategy for a more facile way to discriminate vapours of similar molecules. Vapours can directly influence the electronic states of the systems, resulting in large changes in colour depending on the respective vapour. The method would be applicable to detect diverse organic vapours containing coordination atoms such as nitrogen or oxygen. Very recently, we succeeded in the construction of a vapochromic nickel(II)-quinonoid complex of this type,  $[Ni(HL^{Me})_2]$  (H<sub>2</sub>L<sup>Me</sup> = 4-methylamino-6-methyliminio-3-oxocyclohexa-1,4-dien-1-olate).<sup>11</sup> The crystalline sample of the complex exhibits high-selectivity to methanol vapor changing colours between purple and orange accompanied by the change in the spin-state, although the nickel(II) complex does not emit luminescence.



Scheme 1. Ligand exchange of complex 1 based on solid-vapour reactions.

To demonstrate such a sensing system showing luminescence colour changes, we focused on copper(I)-halide complexes because they are well-known for being inexpensive and strongly emissive complexes, and their emission properties are sensitively affected by the versatile structures and additional ligands.<sup>12</sup> The emission colours of copper(I)-halide complexes with *N*-heteroaromatic ligands can be tuned

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widely from red to blue by varying the ligands.<sup>13,14</sup> These properties suggest the sensing ability of copper(I)-halide complexes to N-heteroaromatic compounds.

Herein, we report a new vapour-responsive system based on luminescent mononuclear copper(I) complexes  $[CuCl(PPh_3)_2(L)]$  (PPh<sub>3</sub> = triphenylphosphine, L = Nheteroaromatic compounds) (Scheme 1). The complexes exhibited remarkable luminescence colour changes in the solid state in response to the vapours of various N-heteroaromatic compounds. We found that the phenomenon occurred due to the ligand exchange of vapour molecules derived from Nheteroaromatic compounds such as pyridine and pyrimidine.

# Experimental

#### Materials

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All commercially available starting materials were used as received and solvents were used without any purification. Unless otherwise stated, all manipulations were conducted in air. Complexes  $[CuCl(PPh_3)_2(4-Mepy)]$  (1) (4-Mepy = 4-methylpyridine),<sup>14</sup> [CuCl(PPh<sub>3</sub>)<sub>2</sub>(py)] (2),<sup>15</sup> and [CuCl(PPh<sub>3</sub>)<sub>3</sub>]·CH<sub>3</sub>CN<sup>16</sup> were prepared according to the literature procedure. The complex 2 was also prepared by a vapour exchange method described below.

Synthesis of [CuCl(PPh<sub>3</sub>)<sub>2</sub>(py)] (2) (py = pyridine) by ligand vapour exposure. Complex 1 (50 mg, 0.070 mmol) was exposed to py vapour overnight. Complex 2 was obtained quantitatively as white powder. The powder X-ray diffraction (PXRD) pattern of the white powder was consistent with the simulated pattern based on the single crystal X-ray analysis of 2 (see the "vapochromic behaviour" paragraph in Results and Discussion). Anal. Calcd for C40H34N2P2ClCu: C, 70.08; H, 5.02; N, 1.99. Found: C, 70.04; H, 5.06; N 2.04.

Synthesis of [CuCl(PPh<sub>3</sub>)<sub>2</sub>(pym)] (3) (pym = pyrimidine) by ligand vapour exposure. Complex 1 (50 mg, 0.070 mmol) was exposed to pym vapour overnight. Complex 3 was obtained quantitatively as pale yellow powder. The PXRD pattern of the powder sample dried in the vacuum was consistent with the simulated pattern based on the single crystal X-ray analysis of 3, although a different pattern was obtained for the sample before drying (Fig. S1). <sup>1</sup>H NMR spectrum indicated that the crystal form before drying included an excess amount of pym as crystal solvent, and the dried form was consistent with the crystalline sample (Fig. S2) Anal. Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>2</sub>P<sub>2</sub>ClCu: C, 68.28; H, 4.87; N, 3.98. Found: C, 68.58; H, 4.96; N 3.85.

Preparation of single crystals of 3. To complex 1 (31.0 mg, 43.3 mmol) was added pym (1 mL). Pale yellow crystals were obtained by slow diffusion of diethyl ether vapour into the solution for one week. Yield. 5.5 mg, 18%. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>CN, Fig. S3(a))  $\delta$ ppm 7.29–7.44 (m, 31 H, phenyl group in PPh<sub>3</sub>+pym-H5), 8.74 (d, J= 4.9 Hz, 2H, pym-H3,6), 9.15 (s, 1H, pym-H2). Anal. Calcd for C40H34N2P2ClCu: C, 68.28; H, 4.87; N, 3.98. Found: C, 68.41; H, 4.73; N3.92.

Synthesis of [CuCl(PPh<sub>3</sub>)<sub>2</sub>(2-Mepyz)] (4) (2-Mepyz = 2methylpyrazine) by ligand vapour exposure. Complex 1 (50 mg, 0.070 mmol) was exposed to 2-Mepyz vapour for one week. Complex 4 was obtained quantitatively as yellow powder. The PXRD pattern of the powder was consistent with the simulated pattern

Preparation of single crystals of 4. To [CuCl(PPh<sub>3</sub>)<sub>3</sub>]·CH<sub>3</sub>CN (101.2 mg, 0.114 mmol) was added 2-Mepyz (1 mL). Yellow crystals were obtained by slow diffusion of diethyl ether vapour into the solution overnight. Yield. 52.0 mg, 63%. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>CN, Fig. S3(b)) δ ppm 2.50 (s, 3H, CH<sub>3</sub>), 7.30–7.42 (m, 30H, PPh<sub>3</sub>), 8.36–8.46 (m, 3H, pyz-H3,5,6). Anal. Calcd for C<sub>41</sub>H<sub>36</sub>N<sub>2</sub>P<sub>2</sub>ClCu: C, 68.61; H, 5.06; N, 3.90. Found: C, 68.60; H, 4.94; N3.85.

#### Measurements.

Luminescence Spectroscopy. The luminescence spectrum of each sample was measured using a JASCO FR-6600 spectrofluorometer at room temperature. The luminescence quantum yield was recorded on a Hamamatsu Photonics C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and 150-W CW Xenon light source. Hamamatsu Photonics A10095-03 non-luminescent quartz sample holder was used for absolute emission quantum yield measurements of the solid samples in air. The accuracy of the instrument was confirmed by the measurement of the quantum yield of anthracene in degassed ethanol solution ( $\Phi$  = 0.27).<sup>17</sup> Emission life time measurements were conducted by using a Hamamatsu Photonics, C4334 system equipped with a streak camera as a photo detector and a nitrogen laser for the 337 nm excitation.

Table 1. Crystal Parameters and Refinement Data for complexes 3 and 4.

	3	4
Formula	$C_{40}H_{34}ICuN_2P_2$	$C_{41}H_{36}CICuN_2P_2$
Formula weight	703.67	717.70
Crystal system	Triclinic	monoclinic
Space group	<i>P</i> -1	P21/c
<i>a</i> (Å)	11.456(1)	9.712(1)
b (Å)	13.009(2)	37.383(5)
<i>c</i> (Å)	13.566(2)	10.869(2)
lpha (deg)	78.890(7)	90
eta (deg)	68.086(6)	115.945(4)
$\gamma$ (deg)	66.559(6)	90
<i>V</i> (ų)	1718.6(5)	3548.3(9)
Т (К)	200(1)	173(1)
Z	2	4
no. of reflections collected	13922	36563
no. of unique reflections	7770	8006
GOF on F <sup>2</sup>	1.034	1.058
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.360	1.343
<b>R</b> <sub>int</sub>	0.0246	0.0676
$R_1(l>2\sigma(l))^a$	0.0343	0.0525

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2}) / \Sigma w(F_{o})^{2}]^{1/2}, w = [\sigma_{c}^{2}(F_{o}^{2}) + (xP)^{2} + (xP)^{2} + (xP)^{2}]^{1/2}$ yP]<sup>-1</sup>,  $P = (F_o^2 - 2F_c^2)/3$ .

Other measurements. The <sup>1</sup>H NMR spectrum of each sample was measured using a JEOL EX-270 NMR spectrometer at room temperature. Elemental analysis was conducted at the analysis centre of Hokkaido University.

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#### X-ray crystallography

Single-crystal X-ray analysis. All single-crystal X-ray diffraction measurements were conducted using a Rigaku Mercury CCD diffractometer with graphite monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å) and a rotating anode generator. Each single-crystal was mounted on a MicroMount Using paraffin oil. The crystal was then cooled using an N<sub>2</sub>-flow type temperature controller. Diffraction data were collected and processed using CrystalClear.<sup>18</sup> Structures were solved by the direct method using SIR-2004<sup>19</sup> for **3** and **4**. Structural refinements were conducted by the full-matrix leastsquares method using SHELXL-97.<sup>20</sup> Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. All calculations were conducted using the Crystal Structure crystallographic software package.<sup>21</sup> Crystallographic data obtained for each complex are summarized in Table 1 and deposited to the Cambridge data centre (CCDC-1519416, 1519417).

**Powder X-ray diffraction measurements.** Powder X-ray diffraction was conducted using a Bruker D8 Advance diffractometer equipped with a graphite monochromator using Cu  $K_{\alpha}$  radiation and one-dimensional LinxEye detector.

#### **Theoretical Calculations**

Density functional theory (DFT) calculations were performed with B3LYP functional<sup>22</sup> and the LANL2DZ basis<sup>23</sup> set using Gaussian 03 program.<sup>24</sup> Molecular structures determined by X-ray crystallographic analysis were used for calculations. Molecular orbitals are shown using Avogadro 1.10.<sup>25</sup>

## **Results and discussion**

**Vapochromic behaviour.** Crystal samples of  $[CuCl(PPh_3)_2(4-Mepy)]$  (4-Mepy = 4-methylpyridine) (1), which were prepared as reported previously,<sup>14</sup> exhibited strong blue emission, as shown in Fig. 1 (a, c, e). Interestingly, upon exposure to the vapours of pyridine (py), pyrimidine (pym), or 2-methylpyradine (2-Mepyz), the emission colour changed from blue to blue-green, yellow, or red, respectively (Fig. 1 (b, d, f)). The NMR spectra and elemental analyses of the exposed samples after drying in a vacuum clearly indicated that the replacement of the 4-Mepy ligand by the other L occurred completely. Therefore, the vapor exposure can be used as a convenient preparation method of the complexes as described in the experimental section.



**Fig. 1.** Photographs of crystals of complex **1** under UV light before (a, c, e) and after vapour exposure of (b) py for 1 day, (d) pym for 2 days, and (f) 2-Mepyz for 3 days, respectively, under ambient vapour pressure at room temperature.

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The vapochromic luminescence was investigated through powder X-ray diffraction (PXRD) measurenieints?3/ the PXRD pattern changes in the case that complex 1 was exposed to py vapour. The PXRD pattern after py vapour exposure (Fig. 2(b)) was completely different from that of 1 (Fig. 2(a)). The pattern was almost consistent with the simulation pattern calculated from the single-crystal X-ray diffraction (SXRD) data of [CuCl(PPh<sub>3</sub>)<sub>2</sub>(py)] (2) Fig. 2(c)),<sup>14</sup> indicating the formation of complex 2 by ligand exchange based on vapour exposure. By exposing the sample after exchange to 4-Mepy vapour again, the PXRD pattern for complex 1 was recovered (Fig. 2(d)). Similar reversible PXRD pattern changes by ligand exchange were observed for pym and 2-Mepyz vapours (Figs. S1 and S4). We confirmed the purity of the complexes  $[CuCl(PPh_3)_2(pym)]$  (3) and [CuCl(PPh<sub>3</sub>)<sub>2</sub>(2-Mepyz)] (4) produced by the vapor exchange on the basis of the elemental analysis (see experimental section).



Fig. 2. Reversible PXRD pattern changes of complex 1; (a) PXRD pattern of complex 1, and (b) that after py vapour exposure. (c) The simulation patterns of complex 2, and (d) PXRD pattern after exposing the sample (b) to 4-Mepy vapour.

**Crystal structures of complexes.** Fig. 3 shows the crystal structures of complexes **3** and **4**. The teterahedral coordination stuctures including chloride, two triphenyl phosphine and a *N*-heteroaromatic ligand are similar to those for complexes **1** and **2** showing the typical mononuclear Cu(I) geometry.<sup>14,15</sup> The coordination of 2-Mepyz at the 4-position of nitrogen (N1) for **4** would be reasonable considering the stric effect of the methyl group (Fig. 3(b)). For both complexes, no special intermolecular interactions can be seen in the crystal, although there are trivial short contacts of Cl…H for **3** and N…H for **4** in the crystal structures, respectively (Fig. S5). Therefore, the luminescence would mainly reflect the electronic properties of the molecular characters.



Fig. 3. Molecular structures of (a) 3 and (b) 4. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are displayed at the 50% probability level. Coordination Bond distances: For 3, Cu1–Cl1 = 2.3510(6), Cu1–P1 = 2.2531(5), Cu1–P2 = 2.2741(6), Cu1–N1 = 2.128(1), For 4, Cu1–Cl1 = 2.3174(8), Cu1–P1 = 2.2764(8), Cu1–P2 = 2.2626(9), Cu1–N1 = 2.136(4).

Luminescence properties. Fig. 4 shows the emission spectra of complexes 1–4 as crystals. The emission maxima ( $\lambda_{max}$ ) of the complexes are 468, 498, 526, and 627 nm for 1, 2, 3, and 4, respectively. The large emission spectral shifts depending on the N-heteroaromatic ligands (L) suggest the involvement of the  $\pi^*$  orbital of L in the emission state. Therefore, this Cu(I) complex system can be a good detector for N-heteroaromatic molecules. Time-dependent density functional theory (TD-DFT) calculations for complexes 3 and 4 indicated that the electron density in the highest occupied molecular orbital (HOMO) was distributed over the Cu and halogen atoms, while that in the lowest unoccupied molecular orbital (LUMO) was localized on L (Fig. S6, Tables S1 and S2), suggesting that the lowest excited states for both 3 and 4 can be assigned to the metal-to-ligand charge transfer (MLCT) states mixed with halide-to-ligand charge transfer (XLCT) states ((M+X)LCT states), as in the case of the complexes 1 and 2.14,26



Fig. 4. Luminescence spectra of 1–4 crystals at 298 K:  $\lambda_{ex}$  = 350 nm for 1, 2 and 3, and  $\lambda_{ex}$  = 400 nm for 4.

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 Table 2. Luminescence properties of crystals 1–4 at 298 K.

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Complex	<b>1</b> <i><sup>g</sup></i>	<b>2</b> <sup><i>h</i></sup>	3 DOI: 10.10	<b>4</b>
$\lambda_{\max}^{a}$ (nm)	468	498	526	627
τ (μs (A <sub>n</sub> )) <sup>b</sup>	5.8 (0.43) 10.7 (0.64)	3.3 (0.13) 12.5 (0.89)	2.3 (0.35) 4.3 (0.69)	3.3 (0.88) 5.5 (0.13)
$arPsi^{c}$	0.99	0.98	0.40	0.09
τ <sub>av</sub> <sup>d</sup> (μs)	9.4	12	3.8	3.7
<i>k</i> r <sup>e</sup> (s <sup>-1</sup> )	1.1 × 105	$8.0 \times 10^{4}$	1.0 × 105	$2.4 \times 10^{4}$
$k_{nr}^{f}$ (s <sup>-1</sup> )	1.1 × 10 <sup>3</sup>	1.6 × 10 <sup>3</sup>	1.5 × 10⁵	2.5 × 10⁵

<sup>*a*</sup> Emission maximum. <sup>*b*</sup> Emission lifetimes. Emission decays were analysed with two components:  $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . <sup>*c*</sup> Photoluminescence quantum yield of the crystal sample. <sup>*d*</sup> Average emission lifetime, which was estimated based on the following equation for the two exponential decay components:  $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$ . <sup>*e*</sup> Radiative rate constant, which was estimated by  $\Phi/\tau_{av}$ . <sup>*f*</sup> Non-radiative rate constant, which was estimated by  $k_f(1 - \Phi)/\Phi$ . <sup>*g*</sup> Ref.14. <sup>*h*</sup> Ref.26.



**Fig. 5.** Plots of  $ln(k_{nr})$  vs. the wavenumber for  $[CuX(PPh_3)_2(L)]$  (L = *N*-heteroaromatics). Red circle: X = Cl<sup>-</sup>, Blue triangle: X = Br<sup>-</sup>, Black square: X = I<sup>-</sup>, The numbers for the complexes **1–4** are shown in the graph. Other data are taken from the previous reports.<sup>26</sup>

The photophysical properties of complexes 1-4 at 298 K are summarized in Table 2. Although the luminescence quantum yields of 1 and 2 are quite high, those of 3 and 4 decreased with the red-shift of the emission wavelength. The trend can be explained roughly by the energy gap law as shown in Fig. 5.<sup>26,27</sup> For the complex 3, however, the slight deviation from the trend suggests additional factors for the nonradiative deactivation of the luminescent state. It would be related to the flexiblity of the crystal structure. In fact, relatively large thermal ellipsoids for some of phenyl groups were found in the X-ray structure of 3 (Fig. 3(a)). The formation of a different crystal structure from that of 3 in the saturated vapour atmosphere of pym and the transformation to the crystal structure of 3 by drying also suggest the flexibility of the crystal structure of 3 (see experimental section).

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To investigate the ligand exchange behaviour, we measured the time-course of emission spectra under vapour exposure. Fig. 6 shows luminescent spectral changes of 1 in the presence of 2-Mepyz vapour. With vapour exposure, the emission intensity of 1 gradually decreased and a new band appeared at a longer wavelength, and finally the spectral change was completed exhibiting the band corresponding to that for complex 4. This suggests the ligand exchange reaction occurred in the solid state followed by structural transformation from 1 to 4. Similar spectral changes of complex 1 were observed in the cases of py and pym vapour exposure, although the reaction times were much faster (Fig. S7). Py, pym, and 2-Mepyz took 2, 11 and 22 h, respectively, to complete the exchange. Such different reaction times can be explained based on the basicity and vapour pressure of L. The pK<sub>a</sub> of the conjugate acids and vapour pressure values (in parentheses, mmHg) at 298 K were reported as follows:<sup>28</sup>6.0 (6), 5.2 (19), 1.3 (18), and 1.5 (9) for 4-Mepy, py, pym and 2-Mepyz, respectively. The low basicity (i.e. low  $pK_a$  of the conjugate acid) and low vapour pressure for 2-Mepyz would result in the slowest exchange among the three.



Fig. 6. Luminescence spectral changes of complex 1 under exposure to 2-Mepyz vapour ( $\lambda_{ex}$  = 350 nm). Inset is an enlarged drawing.

#### Conclusions

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In conclusion, we found a new vapour response system of luminescent mononuclear Cu(I) complexes based on the ligand exchange reaction of N-heteroaromatic compounds. By vapour exposure to complex 1, mononuclear complexes 2, 3, and 4 were easily and purely obtained by the replacement of 4-Mepy with py, pym, and 2-Mepyz, respectively, changing the luminescence colours drastically and reversibly from blue to red. Such ligand exchange reactions would be applicable to various vapours with coordination ability. The wide emission wavelength shifts in exchange reactions are able to recognize N-heteroaromatic vapours for sensing applications. The response time could be improved by the fabrication of thin layers or nano sheets. Therefore, the ligand exchange reactions based on vapour exposure would be useful for easy sensing of VOCs and for a new convenient methodology for the preparation of luminescent complexes. Further studies toward higher response systems of luminescent Cu(I) complexes are in progress.

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