Stepwise Vapochromism Observed for a Simple Terpyridine–Platinum(II) Complex with a Thiocyanato Ligand

Atsushi Kobayashi,[1] Yuki Fukuzawa,[1] Shin-ichiro Noro,[2] Takayoshi Nakamura,[2] and Masako Kato*[1]
[1]*Department of Chemistry, Faculty of Science, Hokkaido University, North-10, West-8, Kita-ku, Sapporo 060-0810*
[2]*Research Institute for Electronic Science, Hokkaido University, North-20, West-10, Kita-ku, Sapporo 001-0020*

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A simple Pt^{II}–terpyridine complex [Pt(NCS)(tpy)](SCN) (tpy = 2,2′:6′,2″-terpyridine) shows distinct two-step vapochromism from red to yellow through dark red in response to methanol vapor. The adsorption isotherm for methanol vapor reveals that the two-step vapochromic behavior originates from breathing-like structural transformations.

Vapochromism, which is reversible color change induced by chemical vapor, is one of the most promising phenomena applicable to chemical sensing applications.[1,2] So far, many efforts have been made to develop new vapochromic meterials.[1,2] In particular, some polypyridine–platinum(II) complexes exhibit excellent chromic behaviors on exposure to chemical vapor such as alcohols and hydrocarbons.[2] It is well known that the Pt^{II}–polypyridine unit can act as a good chromophore whose color strongly depends on the π–π stacking and metallophilic interactions between adjacent units.[2,3] These interactions critically contribute to the energy of the MLCT (metal-to-ligand charge transfer, [$d_{z^2} \rightarrow \pi^*$]) transition.[3] Thus, the structural transformation induced by vapor adsorption should be the key factor for the vapochromism observed for Pt^{II} complexes. Taking advantage of this sensitive chromophore, many vapochromic Pt^{II}–polypyridine complexes have been reported.[2,3] However, there have been few reports concerning the dynamics of the vapochromic behavior. From the view point of sensing application, it is one of the most important points to improve the selectivity and the response to vapor. We have recently designed several vapochromic Pt^{II}–polypyridine complexes and found that some complexes exhibit remarkable vapochromic behaviors.[4] In this paper, we demonstrate that a simple Pt^{II}–polypyridine complex, [Pt(NCS)(tpy)](SCN) (**1**; tpy = 2,2′:6′,2″-terpyridine) shows an interesting two-step vapochromic behavior in response to methanol vapor, and that can be explained by breathing-like transformations. This is the first observation of the two-step transformation although the vapochromic behavior has been reported for several Pt^{II}–polypyridine complexes.

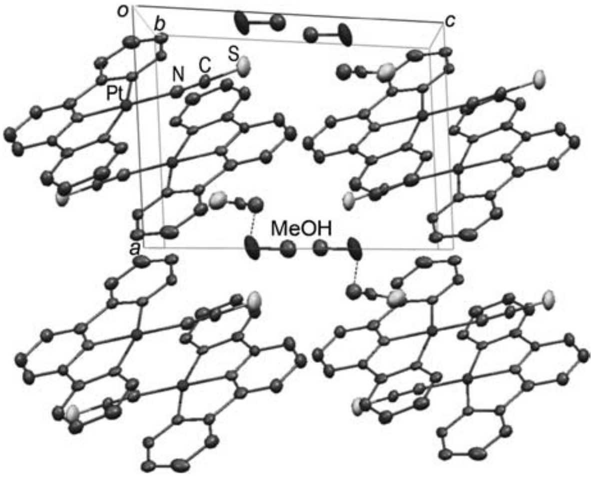

Figure 1. Packing diagram viewed down along the *b* axis. Dotted lines show hydrogen bonds. H atoms are omitted for clarity.

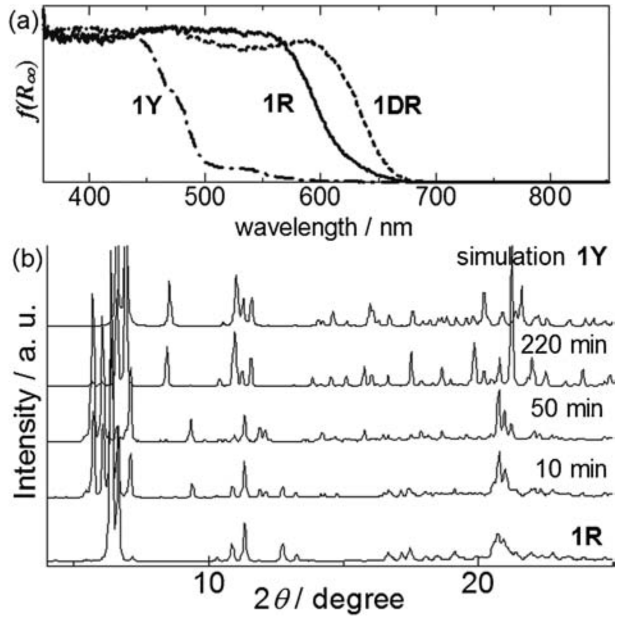

Figure 2. (a) Diffuse reflectance spectra of **1**Y, **1**DR, and **1**Y at room temperature. (b) Exposure time dependence of powder X-ray diffraction pattern of **1**R at 293 K. The pattern on top is a simulation calculated by the crystal structure of **1**Y at 150 K.

The target complex **1** was synthesized according to a method reported previously.[5] Recrystallization from MeOH gave yellow crystal **1**Y. X-ray structural determination for **1**Y revealed that the ambidentate thiocyanato ligand was bound to the Pt^{II} ion by the N atom as shown in Figure 1.[6] The $[Pt(NCS)(tpy)]^+$ units form a dimer with a weak metallophilic interaction between adjacent Pt ions (3.4567(3) Å). In the dimer, two complex units are arranged alternately being related by the inversion center so as to cancel out the dipole moments. Although each dimer is stacked along the *a* axis, the distances between Pt ions are over 6 Å, indicating no metallophilic interaction between dimers. The crystal of **1**Y includes MeOH molecules which are hydrogen-bonded to the N atoms of counter NCS^- anions. It is noteworthy that the MeOH molecules form one-dimensional channels along the *b* axis which should make possible outside access. In fact, the yellow crystals rapidly changed to the red **1**R in air, implying that MeOH was easily released. Interestingly enough, the red color of **1**R returned to yellow after the appearance of a dark red state **1**DR upon exposure to MeOH vapor or by soaking with liquid MeOH. These color changes suggest that the vapochromism of **1** by MeOH vapor occurs in two steps from **1**R to **1**Y via **1**DR, although the conversion from **1**Y to **1**R seems to proceed directly.

In order to get more insight about the vapochromic behavior, powder X-ray diffraction (PXRD) patterns and diffuse reflectance spectra were measured (Figure 2). The dried crystal **1**R showed broad absorption at the wavelengths shorter than around 600 nm in the diffuse reflectance spectrum, and the PXRD pattern was completely different from the simulation pattern of **1**Y. In addition, no signals attributable to MeOH were observed in the ^{1}H NMR spectrum of **1**R. These results prove that the color change from yellow (**1**Y) to red (**1**R) should be derived from the structural transformation due to the loss of MeOH. The two-step change by the exposure to MeOH vapor was confirmed by both diffuse reflectance spectroscopy and PXRD measurements. In the first step, the absorption band shifted to longer wavelength by about 30 nm. The diffraction pattern changed rapidly to one which is similar to neither original **1**R nor simulated pattern of **1**Y. Since the color of the sample was dark red, these spectra and diffraction patterns reflect the structure of **1**DR. The process from **1**R to **1**DR was completed within 1 h. On further exposure to MeOH vapor, the absorption band shifted remarkably in the reverse direction by about 150 nm. Considering the difference between the absorption spectra in MeOH solution and the spectra under exposure to vapor (Figure S1),[7] the weak absorption band at 530 nm observed for **1**Y is attributable to the MMLCT (metal–metal-to-ligand charge transfer) transition. The PXRD pattern also gradually changed to a pattern similar to the simulation of **1**Y, suggesting the structural transformation from **1**DR to **1**Y. To confirm the origin of the vapochromism, the adsorption isotherm of **1**R for MeOH vapor was measured (Figure 3). The isotherm curve showed a sudden increase in vapor uptake at $P/P_0 = 0.55$ and then attained saturation. The saturation amount of MeOH vapor (ca. 1 mol mol^{-1}) corresponds to that observed in the X-ray crystal structure of **1**Y, indicating that the vapochromic behavior of this complex originates from the structural transformation involving MeOH vapor adsorption. Observed large hysteresis and sigmoidal adsorption profile imply that a *breathing*-like structural transformation occurs.[8] For this transformation,[8] the closed form is transformed to an intermediate, and then the intermediate transforms to the adsorbed form. Considering the sigmoidal adsorption profile and the lack of permanent porosity of **1**R (Figure S2),[7] three observed forms, **1**R, **1**DR, and **1**Y are attributable to the closed, intermediate, and full adsorbed forms, respectively. In addition, the red shift of **1**R to **1**DR and the blue shift of **1**DR to **1**Y imply that these two-step structural transformations involve significant shrinkage and elongation of π–π stacking and/or Pt···Pt distances *like a breathing motion*.

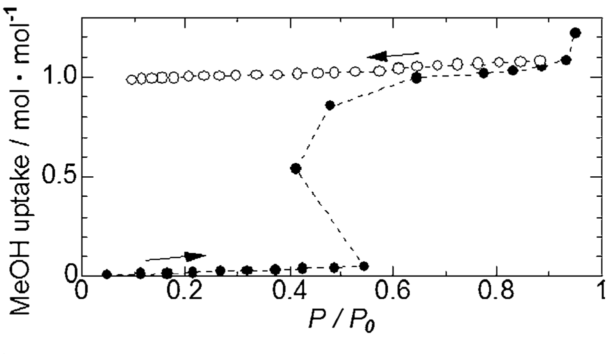

Figure 3. Adsorption isotherm for MeOH vapor of **1**R at 298 K. Closed and open circles show the adsorption and desorption processes, respectively. Dotted line is drawn for a guide.

In summary, we found that a simple Pt^{II}–terpyridine complex, [Pt(NCS)(tpy)](SCN) exhibited distinct two-step vapochromism on exposure to MeOH vapor. The vapochromism from red to yellow via dark red is derived from a breathing-like structural transformation induced by MeOH vapor adsorption. Further work to clarify the adsorption properties and structure in each vapochromic process is in progress.

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6 Crystal data of **1**Y: [Pt(NCS)(tpy)](SCN)•MeOH, $T = 150(1)$ K, $P\bar{1}$ (#2), $a = 8.0530(4)$ Å, $b = 11.2927(2)$ Å, $c = 11.8667(1)$ Å, $\alpha = 61.793(6)°$, $\beta = 86.721(9)°$, $\gamma = 88.373(9)°$, $V = 949.45(5)$ Å^3, $Z = 2$, $\mu(\text{Mo K}\alpha) = 7.6\,\text{mm}^{-1}$, $D_{\text{calcd}} = 2.013\,\text{g cm}^{-3}$. The final R_1 and $wR(F^2)$ were 0.0457 and 0.0694 (all data), respectively. CCDC-741406.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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