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Luminescence Study of Thioamide-based Pincer Palladium Complexes in Poly(vinylpyrrolidone) Matrix

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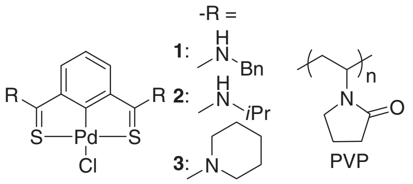
Pincer palladium complexes bearing secondary thioamide units exhibit strong phosphorescence at room temperature upon incorporation into poly(vinylpyrrolidone) matrix; a hybrid film shows reversible switching of luminescence upon exposure to volatile organic compounds.

Square-planar cycloplatinated complexes are often light-emissive, and the use of such light-emissive metal complexes, particularly phosphorescent metal complexes, as emitting materials in light-emitting diodes and luminescent sensors has been intensively investigated.[1–3] Luminescent cyclopalladated complexes are also potential luminescent materials; however, there have been few luminescence studies on cyclopalladated complexes at room temperature.[4] We previously reported that palladium complexes with thioamide-based pincer ligands exhibit strong photoluminescence in glassy frozen matrices.[4b] However, the pincer palladium complexes exhibit hardly any light emission in solution at room temperature. To explore the practical applications of luminescent pincer palladium complexes, enhancement of the room-temperature luminescence from the complex is desired.

Polymer matrices have often been regarded as ambient temperature alternatives to low-temperature organic glasses as media for isolating dispersed species for phosphorescence measurements.[5] Meanwhile, we recently found that photochemical properties of pincer platinum complexes bearing secondary thioamide groups were modulated upon subjection to chemical stimuli.[2g] These observations motivated us to utilize an appropriate polymer matrix to an alternative medium for pincer palladium complexes; this methodology was expected to result in light-emissive hybrid films at room temperature. We here report phosphorescence and vapor-induced switching of luminescence of hybrid films consisting of a pincer palladium complex bearing secondary thioamide units **1** and poly(vinylpyrrolidone) (PVP) (Scheme 1).

The pincer palladium complexes **1**–**3** were prepared from thioamide ligands and K_2PdCl_4 in good yields.[4b,6] All polymer matrices were purchased and used as received. The complex/polymer hybrid films were prepared by dissolving these components with various weight ratios into DMF followed by casting the solution under vacuum.



Scheme 1. Structures of pincer Pd complexes and PVP.

The complex **1** exhibits phosphorescent emission in a glassy frozen matrix of CH_2Cl_2–THF at 77 K ($\lambda_{em} = 505$ nm, $\Phi_{em} = 0.24$, $\tau = 71.8$ µs), whereas the solution shows no emission at room temperature due to molecular distortion which results in nonradiative decay. The complex also shows only weak emission in the solid state ($\lambda_{em} = 682$ nm, $\Phi_{em} < 0.001$), presumably due to the formation of excimers. This situation is quite different when **1** is incorporated into polymer matrices.

In preliminary studies the preparation of hybrid films of **1** and various polymers was surveyed, and we found that the incorporation of **1** into PVP induced markedly enhanced emission ($\lambda_{em} = 532$ nm) at room temperature relative to those of isolated **1**, as shown in Figure 1. Poly(2-ethyl-2-oxazoline) and vinylacetate/vinylpyrrolidone copolymer also produced hybrid films with good light emission. In terms of polymer matrices, other polymers were less effective; only weak emission was observed at room temperature. The luminescence intensity of the **1**/PVP hybrid film increased with increasing content of **1** and reached a maximum at about 10 wt% (the effect of content of **1** is shown in Figure S1).[6] The quantum yield (Φ_{em}) and emission decay lifetime (τ) of the resulting film (9 wt%) were 0.08 and 16 µs, respectively, which are indicative of the phosphorescent emission of **1** even in air at room temperature. The yellowish film with a thickness of 1 µm showed good transparency (>96%) at $\lambda > 470$ nm. XRD analysis of the film only gave broadened amorphous patterns, and no submicron particles were observed by SEM, indicating that **1** is highly

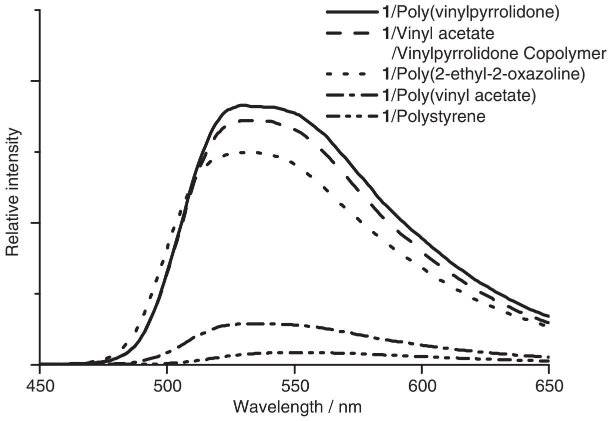


Figure 1. Emission spectra of **1** (9 wt%) in various polymer matrices at room temperature ($\lambda_{ex} = 374$ nm).

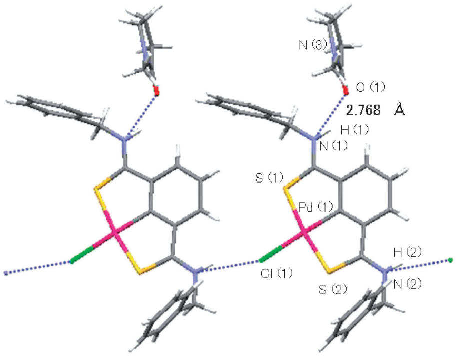


Figure 2. Packing diagram of **1**•NMP.

miscible in PVP. The complex **2** also formed a similar light-emissive hybrid film with PVP. In contrast to **1** and **2**, the related palladium complex **3** bearing a tertiary thioamide group exhibited only weak luminescence in the PVP film. These observations suggest that the presence of the N–H unit of the complexes is essential to the high light-emissive hybrid films at room temperature.

Since PVP has a high T_g (175 °C), the high light emission at room temperature of **1** in PVP is believed to originate from the restricted distortion of the structure at the excited state, which suppresses the nonradiative decay channel of **1** in PVP. A similar explanation has been reported for the stable phosphorescence of cyclometallated Ir complexes in PMMA.[5e] Meanwhile, our observations suggest that the presence of the secondary thioamide is associated with the emissive properties of **1** in PVP. This is reminiscent of the related pincer platinum complexes;[2g] the intermolecular hydrogen-bonding interaction of the secondary thioamide framework causes the photoluminescent properties of the platinum complex to be enhanced. In the present study, the formation of hydrogen bonds between the N–H hydrogen of **1** and the carbonyl group of PVP is thought to increase the rigidity of the ancillary ligand, rendering the relaxation of the excited state of **1** to the ground state via nonradiative decay channels less efficient.[2g,3c,3d,7] The results of IR spectroscopy suggest the hydrogen-bonding interaction between **1** and PVP; the ν(N–H) band of **1** was observed at 3220 cm^{-1} in polystyrene, whereas the ν(N–H) band shifted to 3204 cm^{-1} in PVP. The hydrogen-bonding interaction of **1** with the pyrrolidone unit was also elucidated by X-ray crystallography.[8] Figure 2 shows the crystal structure of **1**•NMP. In the crystal lattice, neither π-stacking interaction of the centered benzene unit nor intermolecular d^8–d^8 interaction is observed with the Pd···Pd separation distance of 8.415 Å. The distance between N atom in the thioamide group and O atom in the NMP molecule (2.768 Å) is in the range of normal hydrogen bonding.[9] Actually, the **1**•NMP crystals exhibit light emission at room temperature ($\lambda_{em} = 517$ nm).

Vapochromic and vapoluminescent materials are attracting increasing attention because of their potential application as practical sensors.[10] The luminescence of the **1**/PVP hybrid film was also sensitive to volatile organic compounds. When chloroform vapor came in contact with the film, the emission intensity immediately decreased approximately tenfold, as shown in Figure 3. The spectral change was a reversible process; the emission intensity was recovered when the film was left in air. We observed similar behaviors for nitromethane, methanol, THF, and DMF. These organic compounds serve as good solvents for PVP; it is reasonable to consider that the swelling of the polymer matrix due to the absorption of volatile molecules disturbs the intermolecular interaction of **1** and PVP.

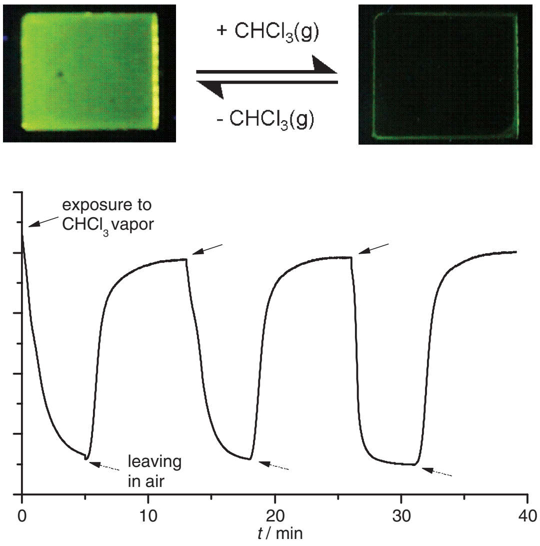


Figure 3. Changes of emission intensity at 532 nm ($\lambda_{ex} =$ 374 nm) for **1**/PVP film upon the cycle of exposure to chloroform vapor and restoration in air.

As described above, the hybrid films consisting of pincer palladium complexes bearing secondary thioamide units and PVP exhibit high light emission at room temperature. Although fundamental studies on the photochemical properties of the hybrid films are still crucial for investigating their new functions and applications in inorganic and polymer chemistry, the present methodology makes it possible to easily prepare light-emissive films at room temperature and thus expand their range of applications.

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8 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-750102. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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