Brilliant reversible luminescent mechanochromism of silver(I) complexes containing *o*-bis(diphenylphosphino)benzene and phosphinesulfide†

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The Ag(I) complex with *o*-bis(diphenylphosphino)benzene shows reversible interconversion between blue-emitting (1b) and green-emitting (1g) materials on grinding and heating; comparison of the structure of 1b with another green-emitting crystals (2) having the same formula suggests the chromism results from intermolecular interactions between adjacent phenylene rings.

Mechanochromism is the phenomenon of color change caused by mechanical grinding or pressing of the solid sample and reversion to the original color by heating or recrystallization, in which the presence of two different pressure-dependent stable or metastable states is essential.[1] Recently, much attention has been paid to the photoluminescent compounds that possess mechanochromic properties in view of unique optical recording devices or sensing materials involving luminescence detection. Some organic mechanochromic substances showing luminescent color change caused by isomerization or variation of molecular packing on grinding have been reported.[2] For luminescence mechanochromism of metal-containing compounds, Pt(II),[3] Zn(II)[4] and Au(I)[5] complexes have been reported, in which difference in the intermolecular interactions is responsible for the change of emission color for the ground samples.

In our groups, extensive studies on the luminescent properties of d^{10} metal complexes involving various phosphines have been reported.[6–8] In these complexes, tetrahedral Pd(0) and Cu(I) complexes have emission bands generally assigned to ^{3}MLCT transition from the metal center to the π* orbital on the ligands. Upon MLCT excitation, the d^9 metallic character causes tetragonal flattening distortion, so luminescent properties based on MLCT transition in d^{10} metal complexes depends on the extent of the distortion.[9] Recently, we have turned our attention to phosphine sulfides in order to prevent oxidation of phosphines and to increase stability of complexes, therefore luminescent properties of mixed-ligand d^{10} complexes with phosphines and phosphine sulfide, *e.g.* $dppaS_2^-$ (Chart 1), have been studied.[10] In these complexes, we have found that a silver(I) complex coordinated by dppbz (= *o*-bis(diphenylphosphino)benzene) and $dppaS_2^-$ ligands, [Ag(dppbz)(dppaS$_2$)], shows emitting color change upon mechanical grinding. Herein, we report the luminescent properties and mechanochromism of this complex.

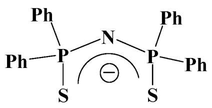

Chart 1 $dppaS_2^-$ ligand.

Treatment of KdppaS$_2$ and dppbz with AgPF$_6$ in CHCl$_3$ readily gives a mixed-ligand complex, [Ag(dppbz)(dppaS$_2^-$)]. The colorless crystals (**1b**) obtained by recrystallization from CHCl$_3$–ether show blue emission upon irradiation of UV-light. X-Ray suitable crystals of **1b** are obtained as prismatic crystals (Fig. S1, ESI†). The structure of **1b** has a distorted tetrahedral geometry coordinated by the $dppaS_2^-$ and dppbz ligands (Fig. 1, black), and no solvent molecules are found in the unit cell.

When the blue-emitting crystals were ground in a ceramic mortar, the white powder obtained emits green luminescence (**1g**). Emission maximum of **1g** occurs at 518 nm, whereas that of **1b** at 458 nm. Since elemental analysis of both **1b** and **1g** gave the same values corresponding to [Ag(dppbz)(dppaS$_2^-$)], the process does not involve adsorption or removal of a solvent molecule as shown in vapochromic systems.[11] Upon treatment of **1g** with drops of CHCl$_3$–hexane (1 : 2), the green luminescence reverted to blue one (Fig. S2, ESI†). Furthermore, emitting color of **1g** returned to blue on heating at 200 °C for 10 minutes (Fig. 2). The thermal properties of **1g** were studied by differential thermal analysis measurement ranging from 25 to 180 °C (Fig. S3, ESI†). The heating profile of **1g** shows a weak exothermic peak at *ca.* 120 °C, which is assigned to the phase transition from **1g** to blue-emitting solid, and a clear endothermic peak at *ca.* 240 °C, which indicates a thermal decomposition.

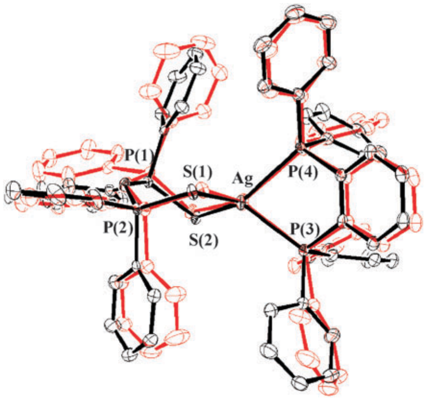

Fig. 1 ORTEP drawings of two forms of [Ag(dppaS$_2^-$)(dppbz)]: **1b** (black) and **2** (red).

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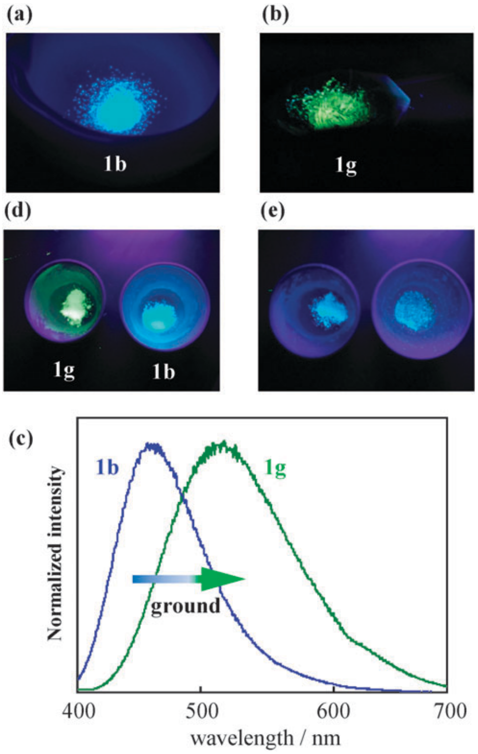

Fig. 2 Emitting color on irradiation of UV-light (365 nm) of **1b** (a) and **1g** (b) and luminescence spectra of **1b** and **1g** (c); emitting color of **1g** and **1b** before heating (d) and after heating at 200 °C for 10 min (e).

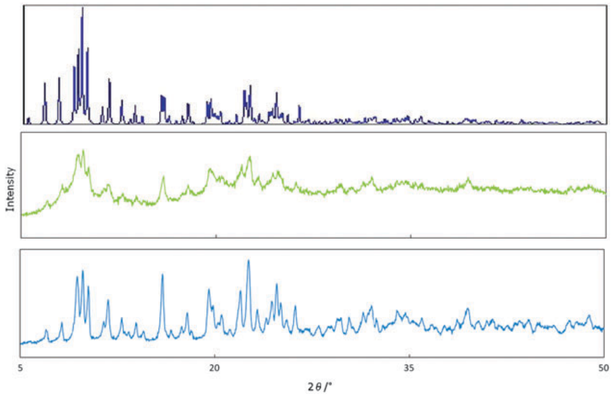

Fig. 3 Simulated XRD pattern of **1b** (upper blue) and observed data of **1g** (middle green) and **1g** after heating at 200 °C (lower pale blue).

Table 1 Selected bonds (Å) and angles (°)

	1b	**2**
Ag–S	2.5805(5), 2.5545(4)	2.5392(10), 2.5341(10)
Ag–P	2.5346(5), 2.5725(6)	2.4916(8), 2.4980(8)
S–P	1.9995(7), 2.0053(6)	2.0064(11), 1.9960(14)
S(1)–Ag(1)–S(2)	109.76(2)	110.06(3)
S(1)–Ag(1)–P(3)	106.71(2)	117.30(2)
S(1)–Ag(1)–P(4)	120.12(2)	115.75(2)
S(2)–Ag(1)–P(3)	124.45(2)	120.78(3)
S(2)–Ag(1)–P(4)	114.74(2)	106.52(3)
P(3)–Ag(1)–P(4)	78.67(2)	83.30(2)
Ag(1)–S(1)–P(1)	95.67(2)	96.09(4)
Ag(1)–S(2)–P(2)	94.15(2)	96.23(4)

A powder X-ray diffraction of **1g** showed only weak and ambiguous reflections (Fig. 3). Some of the weak peaks are assigned to unconverted **1b** crystals because the 2*θ* values of the peaks correspond to those of simulated peaks calculated from the X-ray data of the single crystal of **1b**. After heating the sample of **1g** at 200 °C, some sharp diffraction peaks appeared, which show a better agreement with the simulated pattern of **1b**. The result shows reversible phase conversion occurs from crystal (**1b**) to amorphous (**1g**) on grinding and heating. An attempt to repeat this blue-to-green emission cycles was successful at least five times (Fig. S4, ESI†).

Synthesis of [Ag(dppbz)(dppaS$_2$)] in CH$_3$CN instead of CHCl$_3$ gives needle crystals which show green emission upon irradiation of UV-light (**2**). The space group of **2** is *P*2$_1$/*c* (#14) whereas that of **1b** is $P\bar{1}$ (#2), though the structure of complex molecules in **2** is similar to that of **1b** (Fig. 1, red). The metal–donor bond lengths of **2** are smaller than those of **1b** and thus slight differences of bond angles related to metal center are observed; *e.g.* the bond lengths of Ag–P are 2.5347(5) and 2.5725(6) Å in **2** whereas the ones in **1b** are 2.4916(8), 2.4980(8) Å, and therefore the P–Cu–P chelate angle of **1b** is 78.68(2)°, which is smaller than that of **2** (83.30(2)°) (Table 1). In **1b**, the close distances between the carbon atoms of the phenylene rings of dppbz in adjacent molecules are 3.55 Å (for C(41)–C(39′)) and 3.66 Å (for C(41)–C(38′)), so it suggests that there are noticeable intermolecular interactions between the phenylene rings of the dppbz ligand (Fig. S5, ESI†). In **2**, such interactions are not observed. The shortest distance between phenylene rings is long at ~7 Å (Fig. S6, ESI†).

The emission maximum for **2** in the solid state occurs at 518 nm, which is similar to that of **2** and longer than that of **1b**. In **2**, no change of emission color on grinding was observed. In CH$_2$Cl$_2$ solution, both **1b** and **2** show similar emission at *ca.* 580 nm. Furthermore, the similarity among the absorption spectra of **1b**, **1g** and **2** in solution (Fig. S7, ESI†) suggests that all of the crystal/solid contains structurally similar Ag(I) complex. It was reported that the emission maximum of [Ag(dppbz)$_2$]$^+$ in 2-MeTHF solution occurs at 670 nm, and that the large Stokes shift observed in solution shows that flattening distortion occurs in the MLCT excited state.[12] Therefore, it is suggested that the emissive excited states of [Ag(dppbz)(dppaS$_2$$^-$)] are assigned to MLCT transitions involving the π* orbital of phenylene ring in dppbz ligand, and the green emission is based on the flattened geometry.

A PMMA film containing **1b** (**1-PMMA**), in which dispersion of complex molecules prevents intermolecular interactions, shows similar luminescent color to that of **2** crystal (501 nm, Fig. S8 (ESI†)). In these observations, blue emission is only found for **1b** crystals, where intermolecular π–π interactions involving the phenylene rings are present. So it is suggested that the lack of the intermolecular interaction involving the phenylene rings is responsible for the green emission.

It is uncommon that the π–π interaction involving aromatic rings leads to the blue shift of emission wavelength, because π–π interaction between aromatic rings usually results in a bathochromic shift as seen in the formation of excimer of aromatic systems. For example, emission maximum of

[Pt^{II}(5pb)Cl] (5dpb = 2,6-bis(5-methyl-2-pyridyl)benzene) at 570 nm was shifted to 670 nm on grinding accompanied by the formation of excimer.[3] Two possibilities can be considered for the unique blue shift of the emission of **1b**. First, the intermolecular π–π interaction involving phenylene rings may cause perturbation of energy level for π* orbitals to form specific aggregates. It has been reported that columnar stacks of a tetraphenylpyrene derivative are responsible for blue emission of the solid and that the disruption of the columnar structure by pressure leads to the formation of the green emissive solid with the poorly ordered molecular packing.[2a] However, no remarkable difference between diffuse reflectance spectra of **1g**, **1b** and **2** was observed (Fig. S9, ESI†), so it may not be applicable to this case. Alternatively, it is possible that the intermolecular interaction between adjacent phenylene rings may prevent some distortion of the ligands on excitation, which leads to a small Stokes shift. In this case, the excitation energy of **1g** must be similar to that of **1b**. Actually, excitation maximum of **1g** is similar to that of **1b** (Fig. S10, ESI†). Considering from these results, we propose that mechanical grinding leads to a disruption of intermolecular interaction between phenylene rings of adjacent molecules in **1g** solid to give green emission. **1g** may be in the metastable amorphous phase, and either heating or recrystallization transforms **1g** into more stable **1b** in the mechanochromic system.

Most of the metal complexes showing reversible luminescent mechanochromism reported so far are Au(I) multinuclear complexes, which results from modulation of the aurophilic interactions. The Ag–dppbz system reported herein, which apparently requires different mechanism for the mechanochromism, should provide new mechanistic insights into mechanochromism. Molecular orbital calculation for intermolecular interaction in the Ag–dppbz system may give useful information on the mechanism of the mechanochromism. In addition, our studies underway show that the use of dppbz leads to other complexes showing the luminescent mechanochromism. [Ag(dppbz)$_2$]$^+$ and [Ag$_2$I$_2$(dppbz)$_2$] also show luminescent color change on grinding. As mentioned above, the presence of phenylene ring between the phosphino groups of dppbz must be a key of such mechanochromic properties. Further studies for structural and optical properties of these complexes in detail will elucidate the mechanism for this type of chromism.

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