Systematic structural control of multichromic platinum(II)-diimine complexes ranging from ionic solid to coordination polymer

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Reactions of a Pt(II)-diimine-based metalloligand Na₂[Pt(CN)₂(4,4'-dcbpy)] (4,4'-H₂dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) with alkaline-earth metal salts Mg(NO₃)₂·6H₂O, CaCl₂, SrCl₂·6H₂O, and BaBr₂·2H₂O in aqueous solution gave luminescent complexes formulated as [Mg(H₂O)₆][Pt(CN)₂(4,4'-dcbpy)]·4H₂O (MgPt-4·9H₂O), [[Ca(H₂O)₃][Pt(CN)₂(4,4'-dcbpy)]·3H₂O] (CaPt-4·6H₂O), [[Sr(H₂O)₂][Pt(CN)₂(4,4'-dcbpy)]·(SrPt-4·3H₂O), and [[Ba(H₂O)₂][Pt(CN)₂(4,4'-dcbpy)]·3H₂O] (BaPt-4·5H₂O), respectively. The crystal structures of all MPt-4 complexes were determined by X-ray crystallography. In these structures, the alkaline-earth metal ions are commonly coordinated to the carboxyl groups of the [Pt(CN)₂(4,4'-dcbpy)]²⁻ metalloligand. In the case of MgPt-4·9H₂O, the Mg(II) ion is bound by five water molecules and one oxygen atom of a carboxyl group to form a neutral complex molecule [Mg(H₂O)₆][Pt(CN)₂(4,4'-dcbpy)]. In contrast, the alkaline-earth metal ion and metalloligand form two-dimensional (CaPt-4·6H₂O) and three-dimensional (SrPt-4·3H₂O and BaPt-4·5H₂O) coordination networks, respectively. All fully hydrated complexes exhibited a strong phosphorescence from the triplet π-π* transition state. Luminescence spectroscopy revealed that MgPt-4·9H₂O exhibited interesting multichromic (i.e., thermo-, mechano-, and vapochromic) luminescence, whereas CaPt-4·6H₂O showed only thermochromic luminescence. The other two complexes did not exhibit any chromic behaviour. Combination analysis of powder X-ray diffraction, thermogravimetry, and IR spectroscopy suggests that the dimensionality of the coordination network contributes considerably to both the structural flexibility and luminescence properties; that is, the low-dimensional flexible coordination network formed in MPt-4 complexes with smaller alkaline-earth metal ions enables a structural rearrangement induced by thermal and mechanical stimuli and vapour adsorption, resulting in the observed multichromatic behaviour.

Introduction

One-dimensionally stacked square-planer Pt(II) complexes have attracted considerable attention because of their characteristic coloration, strong luminescence, and interesting chromic behaviours. In this system, the metallophilic interaction between the Pt(II) ions is known to play an important role in determining their unique physical properties. The overlap between the two 5dₓ²orbitals of the Pt(II) ions generates an antibonding dₓ²orbital near the highest-occupied molecular orbital (HOMO) level. Because the energy of this dₓ²orbital strongly depends on the distance between the Pt(II) ions, the colour and/or luminescence of the solid can be widely tuned by manipulating the Pt(II)-Pt(II) distance. In 1995, Mann et al. reported that intermolecular metallophilic interactions between d⁸ metal ions play a critical role in the vapochromic behaviour of these complexes. By exploiting these distance-dependent chromophoric properties, researchers have synthesized many vapochromic Pt(II) complexes. For example, Chen et al. reported the unique vapochromic behaviour of a neutral Pt(II) complex [Pt(Me₂SiC=CbpyC=CSiMe₂)(PhC=C)] that varied the colour depending on the molecular weight of the hydrocarbons. In addition, some Pt(II) and Au(II) complexes have been recently found to exhibit interesting mechanochromic behaviour. However, to the best of our knowledge, there are still few complexes that show the double-, triple-, and multichromic behaviours present in this Pt(II)-diimine series.

We recently reported a chromic coordination polymer (CCP), [[Zn(H₂O)₆][Pt(CN)₂(5,5'-dcbpy)]·H₂O] (ZnPt-5·4H₂O), built from a Zn(II) ion and a Pt(II)-diimine-based metalloligand [Pt(CN)₂(5,5'-H₂dcbpy)] 5,5'-H₂dcbpy = 5,5'-dicarboxy-2,2'-bipyridine, because the structure of coordination polymer (CP) can be easily and widely modified by replacement of metal ions and bridging ligands. We found that the metallophilic interaction between the Pt(II) atoms results in the metalloligands acting as chromic centres even within a relatively rigid coordination network, resulting in thermochromic and insoluble solvatochromic behaviours. In addition, the replacement of bridging metal ion from Zn(II) to alkaline-earth metal ions significantly affected both the vapour-adsorption property and solid-state solvatochromic behaviour. However, the one-
dimensional coordination-network structure built from the alternate arrangement of $\text{M}^{2+}$ ion and the metalloligand $[\text{Pt(CN)}_2(5,5'\text{-dcbpy})]^2-$ is commonly formed, resulting in the limitation of the structural control of the coordination-network structure. Thus, in this work, to control both the chromotopic behavior and coordination-network structure constructed by the Pt(II)-diamine-based metalloligand, we have synthesized four Pt(II)-diamine-based complexes using the isomeric metalloligand, $[\text{Pt(CN)}_2(4,4'\text{-dcbpy})]^2-$ with alkylamine-metal ions, namely, $[\text{Mg(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot \text{H}_2\text{O}$ (MgPt-4-9H$_2$O), $[\text{Ca(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot 3\text{H}_2\text{O}$, (CaPt-4-6H$_2$O), $[\text{Sr(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot \text{H}_2\text{O}$ (SrPt-4-3H$_2$O), and $[\text{Ba(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot 3\text{H}_2\text{O}$ (BaPt-4-5H$_2$O). We found the position of the carboxyl group on the dcbpy ligand significantly affected not only the crystal structures but also the luminescence properties and chromic behaviours, that is, the MgPt-4-9H$_2$O complex, without any infinite coordination network, showed interesting multichromic (thermo-, vapo-, and mechanochromic) luminescence, whereas CaPt-4-6H$_2$O, with a two-dimensional coordination-sheet structure, showed only thermochromic luminescence. The other two coordination polymers (CPs), which featured three-dimensional coordination networks, did not show any chromic behaviour. Although there are many chromic materials that use the Pt(II)-diamine complexes as chromophores,$^{54}$ MgPt-4-9H$_2$O is a very rare example of a material that exhibits triple chromic behaviour. In this paper, we discuss the syntheses, crystal structures, and chromic behaviours of these Pt(II)-diamine-based MPt-4-nH$_2$O complexes on the basis of X-ray structural determinations, powder X-ray diffraction measurements, and luminescence and IR spectroscopy.

**Experimental Section**

**Syntheses**

All starting materials, K$_2$PtCl$_4$, Mg(NO$_3$)$_2$·6H$_2$O, CaCl$_2$, SrCl$_2$·6H$_2$O, BaBr$_2$·2H$_2$O, and 3-methylpyridine were used as received from commercial sources, and the solvents were used without any purification. Unless otherwise stated, all manipulations were performed in air. Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O was prepared according to a published method.$^{60}$

Elemental analysis was performed at the analysis centre in Hokkaido University.

**Synthesis of $[\text{Mg(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot \text{H}_2\text{O}$ (MgPt-4-9H$_2$O):** Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O (10 mg, 17 μmol) was dissolved in water (0.5 ml). To this clear pale-yellow solution, an aqueous solution (0.5 ml) of CaCl$_2$ (2.4 mg, 21 μmol) was added resulting in the gradual emergence of an orange precipitate. After standing at room temperature for 2 weeks, the orange precipitate changed slowly to pale-yellow needle-like crystals. The crystals were collected by filtration and washed with a small amount of water and then dried in air for 1 day to afford MgPt-4-9H$_2$O (4.2 mg) in a 39% yield. One of the single crystals was used for X-ray structural determination. Elemental analysis for MgPt-4-9H$_2$O, calcld.: C 26.38, H 2.85, N 8.79; found: C 26.10, H 2.88, N 8.47. IR (KBr, cm$^{-1}$): 3430 s, 3074 w, 2160 s, 2143 s, 1603 s, 1550 s, 1445 m, 1418 s, 1392 s, 1291 w, 1244 m, 1164 w, 1115 w, 1070 w, 1040 w, 924 w, 782 w, 798 w, 787 m, 716 m, 475 w.

**Synthesis of $[\text{Sr(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot \text{H}_2\text{O}$ (SrPt-4-3H$_2$O):** Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O (20 mg, 35 μmol) was dissolved in water (2 ml). To this clear pale-yellow solution, an aqueous solution (1 ml) of SrCl$_2$·6H$_2$O (9.5 mg, 35.6 μmol) was added resulting in the rapid precipitation of a pale-yellow solid. After stirring for 1 h at room temperature, the precipitate was collected by filtration and washed with a small amount of water and then dried in air for 1 day to afford SrPt-4-3H$_2$O (19 mg) in an 86% yield. Pale-yellow single crystals suitable for X-ray crystallographic analysis were obtained by the diffusion of a SrCl$_2$ ethanol solution into an aqueous solution of Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O. Elemental analysis for SrPt-4-3H$_2$O, calcld.: C 26.65, H 1.92, N 8.88; found: C 26.71, H 1.78, N 8.74. IR (KBr, cm$^{-1}$): 3433 s, 3080 w, 2165 s, 2145 s, 1620 s, 1589 s, 1551 s, 1446 m, 1413 s, 1384 s, 1307 w, 1284 w, 1244 m, 1169 w, 1109 w, 969 w, 1039 w, 918 m, 864 m, 810 w, 798 w, 785 m, 774 w, 713 m, 476 w.

**Synthesis of $[\text{Ba(H}_2\text{O})_2][\text{Pt(CN)}_2(4,4'\text{-dcbpy})]\cdot 3\text{H}_2\text{O}$ (BaPt-4-5H$_2$O):** Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O (20 mg, 35 μmol) was dissolved in water (2 ml). To this clear pale-yellow solution, an aqueous solution (1 ml) of BaBr$_2$·2H$_2$O (12 mg, 36 μmol) was added resulting in the rapid precipitation of a pale-yellow solid. After subsequent stirring for 1 h at room temperature, the precipitate was collected by filtration and washed with a small amount of water and then dried in air for 1 day to afford BaPt-4-5H$_2$O (21 mg) in an 84% yield. Pale-yellow single crystals suitable for X-ray crystallographic analysis were obtained by the diffusion of a BaBr$_2$ ethanol solution into an aqueous solution of Na$_2$[Pt(CN)$_2$(4,4’-dcbpy)]·2H$_2$O. Elemental analysis for BaPt-4-5H$_2$O, calcld.: C 23.46, H 2.25, N 7.82; found: C 23.18, H 2.19, N 7.63. IR (KBr, cm$^{-1}$): 3422 s, 3078 w, 2157 s, 2146 s, 1617 s, 1583 s, 1550 s, 1438 w(sh), 1411 w(sh), 1384 s, 1287 w, 1243 m, 1106 w, 1071 w, 1038 w, 918 w, 861 w, 785 m, 709 m, 478 w.

**Single-crystal X-ray structural determination.**

All single-crystal X-ray diffraction measurements were performed using a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda=0.71069$ Å) and a rotating anode generator. Each single crystal was mounted on a MicroMount with paraffin oil. A nitrogen gas flow temperature controller was used to cool the sample. Diffraction data were collected and processed using CrystalClear.$^{12}$ The structure was solved by a direct method using SIR2004,$^{13}$ and refined by full-matrix least squares using SHELXL-97.$^{14}$ The non-hydrogen atoms in MgPt-4-9H$_2$O, CaPt-4-6H$_2$O and BaPt-4-5H$_2$O were refined anisotropically. In the case of SrPt-4-3H$_2$O, the carbon and nitrogen atoms of the bipyridine rings were refined isotropically and the other non-hydrogen atoms were refined anisotropically due to the poor crystalinity. Disordered water molecules in CaPt-4-6H$_2$O were taken into account using PLATON/SQUEEZE.$^{15}$ Hydrogen atoms were refined using the
riding model. All calculations were performed using the Crystal Structure crystallographic software package. The obtained crystallographic data for each complex are summarized in Table 1.

Table 1 Crystal parameters and refinement data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( T / K )</th>
<th>( a / \AA )</th>
<th>( b / \AA )</th>
<th>( c / \AA )</th>
<th>( \alpha / ^\circ )</th>
<th>( \beta / ^\circ )</th>
<th>( \gamma / ^\circ )</th>
<th>( V / \AA^3 )</th>
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<tr>
<td>( \text{MgPt} \cdot 9\text{H}_2\text{O} )</td>
<td>173(1)</td>
<td>7.1293(19)</td>
<td>7.072(2)</td>
<td>7.3068(19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1353(10)</td>
</tr>
<tr>
<td>( \text{CaPt} \cdot 6\text{H}_2\text{O} )</td>
<td>150(1)</td>
<td>7.1293(19)</td>
<td>7.072(2)</td>
<td>7.3068(19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1353(10)</td>
</tr>
<tr>
<td>( \text{SrPt} \cdot 3\text{H}_2\text{O} )</td>
<td>150(1)</td>
<td>7.1293(19)</td>
<td>7.072(2)</td>
<td>7.3068(19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1353(10)</td>
</tr>
<tr>
<td>( \text{BaPt} \cdot 5\text{H}_2\text{O} )</td>
<td>150(1)</td>
<td>7.1293(19)</td>
<td>7.072(2)</td>
<td>7.3068(19)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1353(10)</td>
</tr>
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Powder X-ray diffraction.

Powder X-ray diffraction (PXRD) measurements at various temperatures were performed using a Rigaku SPD diffractometer at beamline BL-8B at the Photon Factory, KEK, Japan. The wavelength of the synchrotron X-ray was 1.200(1) Å. The sample was placed in a glass capillary with a 0.5-mm diameter. The temperature of the sample was controlled using a nitrogen gas flow variable temperature controller.

Luminescence spectroscopy.

Luminescence spectra were recorded under various conditions on a Jasco FP-6600 spectrofluorometer. The sample temperature was controlled by a JASCO ETC-273 Peltier-type temperature controller. About 1 mg of the sample was placed in a glass capillary with a 0.5-mm diameter. The slit widths of the excitation and emission light were 5 and 6 nm, respectively.

Luminescence quantum efficiency measurements.

The luminescence quantum efficiency of each sample in the solid state was recorded using a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and a 150 W CW Xenon light source.

Luminescence lifetimes.

The luminescence lifetime of each sample was recorded using a Hamamatsu C4780 Picosecond Fluorescence Lifetime Measurement System equipped with a nitrogen laser light source (\( \lambda = 337.1 \) nm).

Thermogravimetric analysis.

Thermogravimetry and differential thermal analysis were performed using a Rigaku ThermoEvo TG8120 analyzer.

IR spectroscopy.

The IR spectrum of each complex was recorded on a Nicolet 6700 FT-IR spectrometer equipped with a Smart-Orbit (Diamond) ATR accessory.

Results and discussion

Crystal structures.

Figure 1(a) shows the molecular structure of \( \text{MgPt} \cdot 9\text{H}_2\text{O} \). The complex crystallized in the triclinic \( P-1 \) space group. The Mg(II) ion is surrounded by one carboxyl oxygen of the \( \{\text{Pt(CN)}_2(4,4'-dcbpy)\}^{2-} \) metalloligand and five water molecules to form a neutral molecule, \( \{\text{Mg(H}_2\text{O})_5\{\text{Pt(CN)}_2(4,4'-dcbpy)\}\} \). The average Mg-O(water) bond distances ranged from 2.06–2.09 Å, which is consistent with the oxygen atoms originating from water molecules as opposed to anionic hydroxide ions. In the \( \{\text{Pt(CN)}_2(4,4'-dcbpy)\}^{2-} \) moiety, all atoms except for the carboxyl oxygens lie on the PtC \(_2\) coordination plane. The bond lengths and angles around the metalloligand are very similar to those in the sodium salt, \( \text{Na}_2\{\text{Pt(CN)}_2(4,4'-dcbpy)\}_2\cdot5\text{H}_2\text{O} \) (see Table S1 in supporting information). In the case of the protonated complex \( \{\text{Pt(CN)}_2(4,4'-H_2dcbpy)\} \), the Pt(II) ions formed a one-dimensional (1-D) stacked structure, and (c) packing diagram viewed down along the \( a \) axis of \( \text{MgPt} \cdot 9\text{H}_2\text{O} \). The coordination spheres of the Pt(II) and Mg(II) ions are shown as blue planes and orange octahedrons, respectively. H atoms are omitted for clarity. Solved water molecules are omitted in (a) and (b) for clarity. The brown, light-blue, and red spheres represent C, N, and O atoms, respectively.
Fig. 2 (a) Asymmetric unit, (b) 1-D stacked structure, and (c) packing diagrams viewed down along the b and (d) a axes of CaPt-4·6H₂O. The coordination spheres of the Pt(II) and Ca(II) ions are shown as blue planes and grayish blue polyhedrons, respectively. The dotted lines represent the effective metallophilic interaction between Pt(II) ions. H atoms are omitted for clarity. Solvated water molecules are omitted in (a), (b), and (c) for clarity. Brown, light-blue, and red spheres represent C, N, and O atoms, respectively.

One unit cell, i.e., five coordinated to the Mg(II) ion and four crystal water molecules. Two of the four crystal water molecules (O10 and O11) are tightly bound by four hydrogen bonds. In contrast, the other two water molecules (O12 and O13) form only one hydrogen bond to the tightly bound crystal water, resulting in larger temperature factors. The latter water molecules form a water channel along the a axis, as shown in Figure 1(c).

Figure 2(a) shows the structure of CaPt-4·6H₂O in one asymmetric unit. The complex CaPt-4·6H₂O crystallized in the monoclinic P2₁/n space group. Only one crystallographically independent Ca(II) ion and the [Pt(CN)₂(4,4'-dcbpy)]²⁻ metalloligand were found in the unit cell. The Ca(II) ion is surrounded by five carboxyl oxygen atoms and three water molecules, resulting in an eight-coordinate structure. The metalloligand [Pt(CN)₂(4,4'-dcbpy)]²⁻ is bound to three Ca(II) ions, as shown in Figure 2(a). The oxygen atoms from one of the
two carboxyl groups (O3 and O4) are bound to a Ca ion in a bidentate fashion. The oxygen atoms of another carboxyl group (O1 and O2) are also coordinated to the Ca ion in a bidentate fashion, but the O1 atom also bridges to the adjacent Ca ion (Figure 2(a)). The [Pt(CN)2(4,4'-dcbpy)]2- units stack with a zigzag-type chain arrangement along the a axis, as shown in Figure 2(b). Owing to an effective metallophilic interaction between the Pt(II) ions, the [Pt(CN)2(4,4'-dcbpy)]2- units are moderately dimerized, with the shortest adjacent Pt-Pt distance being 3.3655(2) Å (Figure 2(b)). As a result of the crosslink of the Ca ions by the metalloligands, an infinite two-dimensional coordination-bonded sheet is formed on the (101) plane, as shown in Figure 2(c). Three coordinated water molecules and two crystal water molecules were found in one unit cell. These crystal water molecules form 1-D water channels along the a axis, as shown in Figure 2(d).

Figure 3(a) shows the structure of SrPt-4·3H2O in one asymmetric unit. The complex SrPt-4·3H2O crystallized in the triclinic P-1 space group. Similar to CaPt-4·6H2O, only one crystallographically independent Sr(II) ion and [Pt(CN)2(4,4'-dcbpy)]2- were found in the unit cell. The Sr(II) ion is coordinated by five carboxyl oxygens, two water molecules, and one cyano nitrogen, resulting in an eight-coordinate structure. The metalloligand [Pt(CN)2(4,4'-dcbpy)]2- is bound to five Sr(II) ions.

The oxygen atoms from one of the two carboxyl groups (O3 and O4) are bound to the Sr ion in a simple bidentate fashion. Although the oxygen atoms of another carboxyl group (O1 and O2) are also coordinated to the Sr ion in a bidentate mode, these oxygen atoms also bridge to the adjacent Sr ions (Figure 3(b)), resulting in the formation of a 1-D coordination chain along the a axis. In contrast to MgPt-4·9H2O and CaPt-4·6H2O, one of the two cyano ligands is bonded to the Sr ion. However, similar to CaPt-4·6H2O, the [Pt(CN)2(4,4'-dcbpy)]2- units stack to form zigzag-type 1-D columns along the a axis, as shown in Figure 3(b). In this column, the shortest distance between Pt(II) ions is 3.374(1) Å, which is slightly longer than that in CaPt-4·6H2O (3.3655(2) Å), suggesting that the metallophilic interaction is slightly weaker in SrPt-4·3H2O. There are no effective π-π interactions between adjacent dcbpy ligands in SrPt-4·3H2O in this column. Owing to both the larger coordination and lower hydration numbers of the Sr(II) ion, this complex has the three-dimensional coordination-bonded rigid structure shown in Figures 3(c) and (d). One of the three water molecules is not directly coordinated to any Sr(II) ions, but are instead hydrogen-bonded to the carboxyl oxygen or cyano nitrogen atoms. In this complex, 1-D water channels are also formed along the a axis.

Figure 4(a) shows the structure of BaPt-4·5H2O in one asymmetric unit. The complex BaPt-4·5H2O crystallized in the monoclinic P21/n space group, and the crystal structure is very similar to that of SrPt-4·3H2O. Similar to CaPt-4·6H2O and SrPt-4·3H2O, only one crystallographically independent Ba(II) ion and [Pt(CN)2(4,4'-dcbpy)]2- were found in the unit cell. The Ba(II) ion is surrounded by six carboxyl oxygens, two water molecules, and one cyano nitrogen, resulting in a nine-coordinate structure. The metalloligand [Pt(CN)2(4,4'-dcbpy)]2- is bound to five Ba(II) ions, as shown in Figure 4(a). The oxygen atoms from one of the two carboxyl groups (O3 and O4) are bound to the Ba ion in a bidentate fashion. Although the oxygen atoms of another carboxyl group (O1 and O2) are also coordinated to the Ba ion in a bidentate mode, these oxygen atoms also bridge to the adjacent Ba ions (Figure 4(a)), resulting in the formation of a 1-D coordination chain along the a axis. Similar to SrPt-4·3H2O, one of the two cyano ligands is bonded to the Ba(II) ion. The [Pt(CN)2(4,4'-dcbpy)]2- units stack to form zigzag-type 1-D columns along the a axis, as shown in Figure 4(b). In this column, the shortest distance between Pt(II) ions is 3.3293(4) Å, which is slightly shorter than that in CaPt-4·6H2O (3.3655(2) Å), suggesting that the metallophilic interaction is more pronounced in BaPt-4·5H2O. There are no effective π-π interactions between
adjacent dcby ligands in BaPt-4·5H₂O in this column. Owing to both the larger coordination and lower hydration numbers of the Ba(II) ion, this complex has the three-dimensional coordination-bonded rigid structure shown in Figures 4(c) and (d). Three of the five water molecules are not directly coordinated to any Ba(II) ions, but are instead hydrogen-bonded to the carboxyl oxygen or cyano nitrogen atoms. In this complex, 1-D water channels are also formed along the a axis.

As discussed above, the heavier and larger alkaline-earth metal ions tend to form higher-dimensional coordination-network structures. This trend is probably due to the larger ionic radius of the metal ions and the smaller hydration enthalpy. As the ionic radius of an ion grows larger, the ion adopts a larger coordination number. In addition, an ion with a smaller absolute value of hydration enthalpy would tend to form an ionic bond with the anionic ligand-like carboxylate rather than a neutral water molecule. Consequently, the variation of the alkaline-earth metal ion in this MPt-4·nH₂O series enables us to modify not only the hydration number but also the rigidity and dimensionality of the coordination-network structure.

Thermochromic luminescence.

Figure 5 shows the temperature dependence of the luminescence spectra of the four complexes, MgPt-4·9H₂O, CaPt-4·6H₂O, SrPt-4·3H₂O, and BaPt-4·5H₂O, at room temperature and 373 K. The photophysical properties of these complexes are summarized in Table 2. The synthesized pale-yellow crystals of MgPt-4·9H₂O and CaPt-4·6H₂O showed greenish yellow luminescence. The spectrum with vibronic structures with a maximum at 498 nm is assignable to the emission from the 3π−σ* state, which is mainly localized on the dcby ligand. Although the emission maxima of the other two complexes were observed at 556 nm, the vibronic structures are almost the same as those of MgPt-4·6H₂O and CaPt-4·6H₂O, implying that they originate from the same 3π−σ* emission. The observed relatively long emission lifetimes, which ranged from 0.27 to 3.25 μs for the MPt-4 complexes, are also consistent with this assignment. As discussed earlier, the shortest intermolecular distances between Pt(II) ions in these complexes suggest that metallophilic interactions are not present in MgPt-4·9H₂O, but are effective in CaPt-4·6H₂O and BaPt-4·5H₂O, which feature shortest intermolecular Pt⋯Pt distances of 3.3655(2) and 3.3293(4) Å, respectively. It is well known that one-dimensionally stacked Pt(II) complexes with effective metallophilic interactions usually exhibit strong phosphorescence from the triplet metal-metal-to-ligand charge-transfer (3MMMLCT) state. Nevertheless, the origin of the emission for each MPt-4 is the 3π−σ* state, implying that the metallophilic interactions in CaPt-4·6H₂O and BaPt-4·5H₂O are not strong enough to change the emission origin from the 3π−σ* to the 3MMMLCT state. In fact, the relatively long emission lifetimes of about 1 μs and their characteristic vibronic structures in the emission spectra are quite comparable to the emission from the 3π−σ*(bpy) state observed for [Pt(CN)₂(dC₆H₄py)] (dC₆H₄py = 4,4’-dinonyl-2,2’-bipyridine) in a CHCl₃ solution. It is noteworthy that after heating to 373 K, the luminescence spectra of MgPt-4·9H₂O and CaPt-4·6H₂O changed to spectra similar to those of the other two MPt-4 (M = Sr²⁺ and Ba²⁺) featuring two main emission bands at 560 and 602 nm. The emission lifetime of MgPt-4·9H₂O after heating at 373 K was about 0.3 μs, which is about one-tenth of the lifetime of the room-temperature MgPt-4·9H₂O and comparable to that of SrPt-4·3H₂O (see Table 2). In contrast, SrPt-4·3H₂O and BaPt-4·5H₂O showed almost temperature-independent luminescence.

In both cases, the similar vibronic structures observed in the spectra suggest that the emission origin, i.e., the 3π−σ* state, remains unchanged.

In order to account for the mechanisms of the thermochromic luminescence, thermogravimetric (TG) analysis and powder X-ray diffraction (PXRD) measurement were performed. TG analyses of the four MPt-4·nH₂O complexes revealed that heating at 373 K removed almost all of the water molecules to form anhydrous MPt-4 (see Figure S1). Figure 6 shows the changes in the PXRD patterns of MgPt-4·9H₂O and CaPt-4·6H₂O. The PXRD patterns observed for anhydrous MgPt-4 and CaPt-4 after drying MgPt-4·9H₂O and CaPt-4·6H₂O at 373 K for 1 day were completely different to those of the original hydrates. In contrast, the PXRD pattern of BaPt-4·5H₂O was not changed after increasing the temperature (see Figure S2). Thus, the thermochromic luminescences of both complexes are

### Table 2 Photophysical properties of MPt-4·nH₂O complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_em (RT) / nm</th>
<th>λ_em (100 °C) / nm</th>
<th>τ_em (RT) / μs</th>
<th>Φ_em (RT) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgPt-4·9H₂O</td>
<td>498</td>
<td>560</td>
<td>3.25</td>
<td>0.21</td>
</tr>
<tr>
<td>CaPt-4·6H₂O</td>
<td>498</td>
<td>562</td>
<td>1.47</td>
<td>0.27</td>
</tr>
<tr>
<td>SrPt-4·3H₂O</td>
<td>557</td>
<td>555</td>
<td>0.27</td>
<td>0.09</td>
</tr>
<tr>
<td>BaPt-4·5H₂O</td>
<td>555</td>
<td>557</td>
<td>0.48</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* λ_em = 400 nm. 

** Φ_em = 337.1 nm.
considered to be driven by a structural transformation caused by the release of the water molecules. The emission maxima and vibronic structures of MgPt-4 and CaPt-4 are comparable and similar to those of BaPt-4·5H2O and SrPt-4·3H2O, implying that the structures of anhydrous MgPt-4 and CaPt-4 may be similar to that of BaPt-4·5H2O, which has a 3-D coordination-bonded network structure. This structural transformation would affect the rigidity of the crystal lattice, leading to a change in the vibronic structures of their luminescence spectra.

Vapochromic and mechanochromic luminescence of MgPt-9H2O.

In this section, we discuss the multichromic luminescence of MgPt-4·9H2O in detail because it is the only complex that exhibits vapochromic and mechanochromic behaviours. Figure 7 shows the luminescence spectral changes in MgPt-4·9H2O after grinding for 10 min and after exposing the samples to MeOH vapour for 1 day. The luminescence spectrum of the as-synthesized crystals changed from a greenish yellow \( \pi-\pi^* \) emission to a yellow emission centered at 537 nm with a shoulder at 607 nm after exposure to the MeOH vapour. The colour and emission were also changed to a reddish orange emission centered at 624 nm after mechanical grinding of the crystals, as shown in Figures 7 and 8. Interestingly, after exposing the crushed sample to MeOH vapour, it had almost the same yellow emission, with a maximum at 537 nm, as the as-synthesized crystals that had been exposed to MeOH vapour. The original emission of MgPt-4·9H2O was gradually recovered by immersing these samples in water, even though MgPt-4·9H2O is nearly insoluble in water. As summarized in Scheme 1, these results indicate that MgPt-4·9H2O is a multichromic (vapochromic, mechanochromic, and thermochromic) luminescent complex.

To investigate the mechanism of the vapochromic and mechanochromic behaviours, we measured PXRD patterns under various conditions. Figure 9 shows the changes in the PXRD pattern of MgPt-4·9H2O upon mechanical grinding and exposure to MeOH vapour. Both the as-synthesized and crushed crystals showed almost the same diffraction patterns, suggesting that the

- **Fig. 6** Temperature dependence of PXRD patterns of (a) MgPt-4·9H2O and (b) CaPt-4·6H2O. The black and red lines represent the diffraction patterns at room temperature and 373 K, respectively.
- **Fig. 7** Luminescence spectral changes in MgPt-4·9H2O by mechanical grinding and exposure to MeOH vapour \( (\lambda_{ex} = 400 \text{ nm}) \). The black and blue lines represent the spectra of as-synthesized and crushed crystals, respectively, whereas the dotted and solid lines represent the spectra before and after exposure to MeOH vapour for 1 day at room temperature, respectively.
- **Fig. 8** Mechanochromic behaviour of MgPt-4·9H2O. The upper and lower images are bright-field and luminescence images of (a, c) as-synthesized and (b, d) crushed crystals of MgPt-4·9H2O, respectively.
- **Scheme 1** Schematic diagram summarizing the multichromic behaviour of MgPt-4·9H2O.
The long-range structure of MgPt-4·9H₂O was retained after mechanical grinding. It may be noted that the peak intensities and widths in the crushed sample were weaker and broader than those of the as-synthesized crystals in spite of the fact that both originated from the same amount of sample, which implies that the crystalline MgPt-4·9H₂O was partly transformed to an amorphous solid by mechanical grinding. A remarkable change was observed in the IR spectrum of the crushed MgPt-4·9H₂O. As shown in Figure 9(a), the overall spectral features of the as-synthesized and crushed crystals were quite similar. However, the ν(C=N) mode of the cyano ligand was observed as two bands in the as-synthesized crystals, whereas it was observed as two bands with a shoulder at 2138 cm⁻¹ in the crushed sample, which was not observed for any of the other crushed MPt-4·nH₂O crystals (see Figure S3). In addition, the elemental analysis of the crushed sample revealed that its chemical composition is the same as that of the as-synthesized MgPt-4·9H₂O (see supporting information). Thus, these results suggest that the observed mechanochromic behaviour of MgPt-4·9H₂O originates from the local structural change around the cyano ligand which might enhance the intermolecular metalophilic and/or π-π stacking interactions between the adjacent Pt(II) metalloligands. The PXRD pattern of as-synthesized MgPt-4·9H₂O also significantly changed upon its exposure to MeOH vapour. As shown in Figure 9, new intense diffraction peaks appeared at 6.2°, 7.3°, and 9.4°. A similar diffraction pattern was observed for the sample obtained from the exposure of crushed MgPt-4·9H₂O to MeOH vapour, suggesting that the structures of as-synthesized and crushed MgPt-4·9H₂O were the same after exposure to MeOH vapour. In the IR spectrum of MgPt-4·9H₂O that was exposed to MeOH vapour, the broad band assigned to the ν(O-H) mode of water molecules, appearing at 3400 cm⁻¹, seems to shift to a lower wavenumber as shown in Figure 10(b). New bands, assignable to the C-H and C-O stretching modes of the adsorbed MeOH, were observed at 2944, 2829, and 1033 cm⁻¹, respectively, which are comparable to that of normal liquid MeOH. Similarly, under exposure to the as-synthesized MgPt-4·9H₂O to methanol-d₄ vapour at room temperature, the bands assigned to ν(O-D) and ν(C-O) bands of methanol-d₄ were also observed at around 2493, 2074 and 985 cm⁻¹ and gradually increased, those energies are quite comparable to that of normal liquid of methanol-d₄ (see Figure S4). These results suggest that the adsorbed MeOH molecule was not directly bonded to the Mg(II) ion. In the case of the crushed sample, the characteristic ν(C=N) band at 2138 cm⁻¹ disappeared after exposure to MeOH vapour. In addition, elemental analysis of the sample obtained after the exposure of MgPt-4·9H₂O to MeOH vapour for 1 day also suggests that three of the nine water molecules were replaced by one MeOH molecule to form MgPt-4·6H₂O·MeOH (see supporting information). In the TG-DTA analysis of the sample exposed to MeOH vapour, the gradual weight loss about 20.0% (at 400 K) was observed, which corresponds to the removal of all solvated water and methanol molecules in MgPt-4·6H₂O·MeOH. In addition, three endothermic peaks at 308, 325, and 335 K were observed for the methanol exposed sample, whereas the original MgPt-4·9H₂O showed only one endothermic peak at 321 K (see Figure S5). Thus, the vapochromic behaviour of MgPt-4·9H₂O is thought to originate from the exchange of water with MeOH, which induces a molecular rearrangement of the solid state. As mentioned above, four of the nine water molecules were not
bonded to the Mg(II) ion and formed 1-D water channels along the a axis, which may enable their easy exchange with MeOH. Although we have not yet succeeded in the structural determination of MgPt-4·4H$_2$O·MeOH, its emission energy and spectral shape suggest that the molecular rearrangement induced by guest exchange may enhance the intermolecular metallophilic and/or π-π stacking interaction, leading to a red shift of the emission band.

Effect of the position of carboxyl group in the metalloligand.

As mentioned in Introduction, we have previously reported the structures and chromic behaviours of the luminescent coordination polymers, MPt-5·nH$_2$O built from divalent M$^{2+}$ ions (M = Zn$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$) and the isomeric metalloligand [Pt(CN)$_2$(5,5'-dcbpy)]$^{2-}$. In this section, we discuss the effect of the position of carboxyl group on the metalloligand based on the comparison between MPt-5 and MPt-4 systems.

In the structures of MPt-5·nH$_2$O, one-dimensional coordination-bonded chain structure constructed by the alternate arrangement of M$^{2+}$ ion and the metalloligand [Pt(CN)$_2$(5,5'-dcbpy)]$^{2-}$ are commonly formed and the metallophilic interaction between Pt(II) ions is effective in all MPt-5·nH$_2$O complexes (scheme 2(a)). The bridging M$^{2+}$ ions are bound by two carboxylate groups of the metalloligand at the axial position and several water molecules in the equatorial plane. The hydration numbers (n = 4 - 5) of MPt-5 complexes are almost independent of the M$^{2+}$ ion. By contrast, the crystal structures of MPt-4 complexes strongly depend on the M$^{2+}$ ion (scheme 2(b)). Except for the MgPt-4·9H$_2$O, the bridging M$^{2+}$ ions are surrounded by two or three carboxylate groups of the metalloligand, and the hydration numbers of MPt-4 complexes strongly depend on the M$^{2+}$ ion and are in the range from 3 to 9. It should be emphasized that the intermolecular metallophilic interaction in the MPt-5 system is thought to be effective in the uniformly stacked Pt(II)-complex columns, whereas it is only effective in the dimerized structure in all the fully-hydrated MPt-4·nH$_2$O complexes except for the MgPt-4·9H$_2$O in which there is no metallophilic interaction. In addition, the sodium salt of the metalloligand, Na$_2$[Pt(CN)$_2$(4,4'-dcbpy)]$·$5H$_2$O has also no metallophilic interaction. Consequently, emission properties of MPt-5 and MPt-4 systems are quite different to each other, i.e., the MPt-5 complexes exhibit the red emission derived from the $^3$MMLCT state with relatively short emission lifetime ($\tau_{em}$ = 25 - 69 ns) with small quantum yields ($\Phi_{em}$ = 0.05 - 0.12), whereas the MPt-4 complexes shows the green to yellow emission originating from the $^3\pi-\pi^*$ excited state with long emission lifetime ($\tau_{em}$ = 0.27 - 3.27 µs) and large quantum yields ($\Phi_{em}$ = 0.09 - 0.27). In addition, the MPt-5 complexes commonly exhibit interesting solid-state solvatochromic behaviour driven by the adsorption/desorption of the hydration water molecules, whereas the chromic behaviours of MPt-4 complexes strongly depend on the M$^{2+}$ ion as discussed above. These differences clearly indicate that the position of the carboxyl group attached on the bipyridine ligand plays an important role on these MPt systems. Considering the fact that the acid-dissociation constants of 4,4'-H$_2$edcbpy and 5,5'-H$_2$edcbpy are very close to each other, the positional difference of the coordination-bonding site gives considerable effects on the coordination-network structures including the intermolecular metallophilic interaction. In addition, more negative reduction potential of the 4,4'-H$_2$edcbpy ligand than that of 5,5'-H$_2$edcbpy may affect the emission properties of these Pt(II)-diimine-based complex salts.

Conclusion

We synthesized four new Pt(II)-diimine-based complex salts with alkaline-earth metal ions, namely, [{[Mg(H$_2$O)$_6$][Pt(CN)$_2$(4,4'-dcbpy)]}$·$4H$_2$O] (MgPt-4·9H$_2$O), [{[Ca(H$_2$O)$_6$][Pt(CN)$_2$(4,4'-dcbpy)]}$·$3H$_2$O] (CaPt-4·6H$_2$O), [{[Sr(H$_2$O)$_6$][Pt(CN)$_2$(4,4'-dcbpy)]}$·$3H$_2$O] (SrPt-4·3H$_2$O), and [{[Ba(H$_2$O)$_6$][Pt(CN)$_2$(4,4'-dcbpy)]}$·$3H$_2$O] (BaPt-4·5H$_2$O). Single-crystal X-ray structural determination revealed that there were water channels in their crystals and that the metallophilic interaction between Pt(II) ions was negligibly weak in MgPt-4·9H$_2$O and moderate in the other three MPt-4·nH$_2$O, which formed dimerized structures. There was no coordination network in the MgPt-4·9H$_2$O, but two- and three-dimensional rigid coordination networks were formed in CaPt-4·6H$_2$O and the other two complexes, respectively. These structures are quite different to the Pt(II)-diimine-based MPt-5 system with the isomeric metalloligand, [Pt(CN)$_2$(5,5'-dcbpy)]$^{2-}$. All of the complexes exhibited $^3\pi-\pi^*$ emission with similar vibronic structures. MgPt-4·9H$_2$O was found to be tripichromatic (thermo-, mechano-, and vapochromic) luminescent materials. CaPt-4·6H$_2$O showed only the thermochromic luminescence and the other two complexes that featured heavier alkaline-earth metal ions did not exhibit any chromic behaviour. The thermochromic luminescence of the former two complexes is
mainly derived from the adsorption/desorption of water. The large amount of water molecules included in MgPt-4·H₂O may enable it to respond to guest exchange and mechanical grinding, leading to the interesting multichromic luminescence. Further study on the fine tuning of the structural flexibility to control the multichromic behaviour is now in progress.

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Notes and references


