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Coordination-Induced Self-Assembly of a Heteroleptic Paddlewheel-Type Dirhodium Complex

Kazuki Arakawa ¹, Natsumi Yano ² , Nanako Imasaki ¹, Yoshihiro Kohara ¹, Daiki Yatsushiro ¹, Daiki Atarashi ¹, Makoto Handa ¹  and Yusuke Kataoka ^{1,*} 

¹ Department of Chemistry, Graduate School of Natural Science and Technology, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan; n18m602@matsu.shimane-u.ac.jp (K.A.); n19m602@matsu.shimane-u.ac.jp (N.I.); s161052@matsu.shimane-u.ac.jp (Y.K.); n18m618@matsu.shimane-u.ac.jp (D.Y.); atarashi@riko.shimane-u.ac.jp (D.A.); handam@riko.shimane-u.ac.jp (M.H.)

² Special Course of Science and Engineering, Graduate School of Natural Science and Technology, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan; s179802@matsu.shimane-u.ac.jp

* Correspondence: kataoka@riko.shimane-u.ac.jp

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Abstract: A novel heteroleptic paddlewheel-type dirhodium (Rh₂) complex [Rh₂(O₂CCH₃)₃(PABC)] (**1**; PABC = *para*-aminobenzenecarboxylate), which has an amino group as a potential donor site for coordination with the metal ion, was synthesized and characterized by ¹H NMR, ESI-TOF-MS, infrared spectra, and elemental analysis. The slow evaporation of *N,N*-dimethylformamide (DMF)-dissolved **1** produces the purple-colored crystalline polymeric species [Rh₂(O₂CCH₃)₃(PABC)(DMF)]_n (**1P**). Single-crystal and powder X-ray diffraction analyses, as well as thermo-gravimetric analysis, clarified that **1P** formed a one-dimensional polymeric structure, in which the two axial sites of the Rh₂ ion in **1P** are coordinated by a DMF molecule and an amino group of the PABC ligand of the neighboring molecule **1**, by coordination-induced self-assembly (polymerization) with an Rh-amino bond. The reversible structural change (self-assembly and disassembly transformations) between the discrete species [Rh₂(O₂CCH₃)₃(PABC)(DMF)₂] (**1D**; green solution) and the polymeric species **1P** (purple solid) was accompanied by a color change, which easily occurred by the dissolution and evaporation procedures with DMF.

Keywords: coordination polymer; self-assembly; crystal structure; paddlewheel-type complex; dirhodium complex

1. Introduction

Paddlewheel-type dirhodium (Rh₂) complexes have been attracting considerable interest owing to the basic understanding of their molecular geometries and electronic structures with metal-metal bonds [1] as well as their intriguing properties as antitumor agents [2–4], chemical sensors [5–7], and catalysts for various types of organic reactions [8–11] and photochemical and electrochemical hydrogen evolution from aqueous solutions [12–14]. A considerable number of experimental and theoretical studies have adequately evaluated the synthesis, molecular geometries, and electronic structures of homoleptic Rh₂ complexes with the same bridging carboxylate ligands, [Rh₂(O₂CR)₄L₂] (O₂CR = bridging carboxylate ligand, L = axial coordinated ligand) [1,15–21]. However, heteroleptic Rh₂ complexes with mixed bridging carboxylate ligands, [Rh₂(O₂CR)_n(O₂CR')_{4-n}L₂] (n = 1–3), are very limited [22,23]; thus, related research is also insufficient.

Recently, paddlewheel-type Rh₂ complexes have been utilized as secondary building units (SBUs) for supra-molecular complexes [24,25], such as coordination polymers (CPs) [26–30] and

metal-organic frameworks (MOFs) [31–35], owing to their water and thermal stabilities. There are two conventional synthetic strategies for the production of Rh₂-SBU-based CPs and MOFs. The first strategy is the ligand-exchange reaction between the equatorial carboxylate ligands of the Rh₂ complex precursor and organic poly-carboxylic acids at high temperature [14,31–34]. The second strategy is the coordination-induced self-assembly reaction, in which polydentate imine ligands, such as pyridine and 4,4'-bipyridine [26–29,35], are coordinated with the axial sites of Rh₂ complexes. In general, two synthetic strategies are applied to homoleptic Rh₂-SBUs with the same bridging carboxylate ligands. To our knowledge, CPs and MOFs constructed from heteroleptic Rh₂-SBUs with mixed carboxylate ligands have not been reported.

With this background in mind, this study integrates the two abovementioned synthetic strategies to establish a new synthetic strategy for the synthesis of Rh₂-SBU-based CPs and MOFs. Specifically, we prepared a new heteroleptic Rh₂ complex [Rh₂(O₂CCH₃)₃(PABC)] (**1**; PABC = *para*-aminobenzenecarboxylate), in which the amino group of the PABC ligand is coordinated with the axial sites of the Rh₂ unit. As shown in Figure 1, although complex **1** exists as a discrete molecular structure [Rh₂(O₂CCH₃)₃(PABC)(DMF)₂] (**1D**) in *N,N*-dimethylformamide (DMF), it was easily self-assembled to form a one-dimensional polymeric structure [Rh₂(O₂CCH₃)₃(PABC)(DMF)]_n (**1P**) by the evaporation of the DMF solvent. Evidently, the polymeric species **1P** can be re-dissolved in DMF, which indicates that the self-assembly and disassembly transformations between **1D** and **1P** easily occurred by the dissolution and evaporation procedures with DMF. We believe that this study affords a new strategy for the construction of self-assembled CPs with paddlewheel-type Rh₂-SBUs.

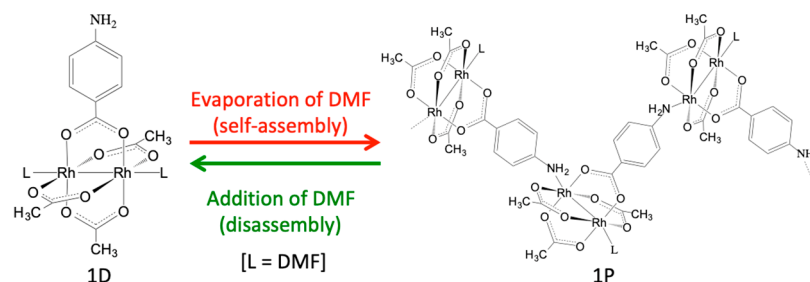


Figure 1. Self-assembly and disassembly transformations between [Rh₂(O₂CCH₃)₃(PABC)(DMF)₂] (**1D**) and [Rh₂(O₂CCH₃)₃(PABC)(DMF)]_n (**1P**).

2. Materials and Methods

2.1. General

All materials, solvents, and gases used in this study were purchased from commercial suppliers and were used without further purifications. [Rh₂(O₂CCH₃)₄(H₂O)₂] was prepared according to the literature [36]. Proton nuclear magnetic resonance (¹H NMR) spectra were performed with a JEOL-500SS (500 MHz) spectrometer (Tokyo, Japan) with DMF-*d*₇ as the solvent. Chemical shifts were referenced to residual DMF (δ = 2.75 ppm). Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was performed with a Bruker micrO-TOF II analyzer (Billerica, MS, USA). The instrument was calibrated with a solution of sodium formate. Infrared spectra were obtained with a JASCO FT/IR 6300 spectrometer equipped with a JASCO ATR PRO ONE module (Tokyo, Japan). Powder X-ray diffraction analysis was performed on a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (Tokyo, Japan). Thermo-gravimetric (TG) analysis was conducted with a MAC Science TG-DTA 2000S (Billerica, MS, USA) with a heating rate of 4 K/min under a nitrogen atmosphere. The UV-visible absorption spectrum in DMF was recorded with a JASCO V-670 spectrometer (Tokyo, Japan). The diffuse reflectance spectrum was measured with a JASCO V-670 spectrometer equipped with a JASCO ISN-923 integrating sphere (Tokyo, Japan). Elemental analysis was conducted on a Yanaco CHN CORDER MT-6 installed at Shimane University, Japan.

2.2. Synthesis of $[Rh_2(O_2CCH_3)_3(PABC)]$ (**1**)

A mixture of $[Rh_2(O_2CCH_3)_4(H_2O)_2]$ (191.2 mg, 0.40 mmol), HPABC (54.8 mg, 0.40 mmol), and CH_3CN (20.0 mL) was placed into the autoclave and sealed under an Ar atmosphere. Then, the reaction mixture was heated at 413 K for 6 h. The resulting solution was evaporated until dry, and the residue was purified by silica-gel column chromatography (eluent: 5% MeOH in $CHCl_3$). After the evaporation of the solvent, the green-colored residue was collected and dried for 3 h at 353 K. Yield: 32.9 mg (0.0634 mmol, 15.9%). Anal. calc. for $Rh_2C_{13}H_{15}NO_8$: C, 30.08%; H, 2.91%; N, 2.70%. Found: C, 29.64%; H, 3.26%; N, 2.81%. 1H NMR (500 MHz, $DMF-d_7$, 300 K): δ = 7.55 (d, 2H, PABC-CH), 6.54 (d, 2H, PABC-CH), 5.78 (s, 2H, PABC-NH₂), 1.79 (s, 3H, *trans*-O₂CCH₃), 1.71 (s, 6H, *cis*-O₂CCH₃). ESI-TOF-MS: calc. for $[M+Na]^+$: 541.8800 *m/z*; found 541.8783 *m/z*. Infrared (ATR, cm^{-1}): 3273(w), 3184(w), 2985(w), 1596(s), 1575(s), 1500(w), 1402(s), 1345(m), 1253(m), 1176(m), 1097(w), 1020(m), 1003(m), 893(m), 862(m), 848(w), 806(w), 773(m), 696(s), 659(m), 626(w), 591(w).

2.3. Single-Crystal X-Ray Diffraction Analysis

Single crystals of **1P** suitable for single-crystal X-ray diffraction analysis were obtained by the slow evaporation of the DMF solution of **1**. The X-ray diffraction data of **1P** were collected at 150 K using a RIGAKU Mercury system equipped with a rotating-anode X-ray generator with Mo K α radiation (λ = 0.71075 Å) installed at the Institute of Molecular Science and were processed using the RIGAKU CrystalClear-SM Expert 2.0 program. The structure of **1P** was solved by the direct method SIR-2011 [37] and was refined using the full-matrix least-squares technique F^2 with SHELXL2014 [38] equipped in the RIGAKU CrystalStructure 4.3 software. Non-hydrogen atoms were refined with anisotropic displacement, and hydrogen atoms were located at the calculated positions and were refined as riding models. The crystal data and details of the data collection and refinement of **1P** are summarized in Table 1 and can be obtained as a CIF from the Cambridge Crystallographic Data Center (CCDC). The deposition number of **1P** is CCDC-1973889.

Table 1. Crystallographic and refinement data of **1P**.

Compound	$[Rh_2(O_2CCH_3)_3(PABC)(DMF)]_n$
Formula	$C_{16}H_{22}N_2O_9Rh_2$
Mr (g mol ^{−1})	592.17
Crystal system	Monoclinic
Space group	$P 2_1/c$
a (Å)	8.1042(11)
b (Å)	14.3559(18)
c (Å)	17.696(3)
β (°)	103.077(3)
V (Å ³)	2005.4(5)
Z	4
D_{calc} (g cm ^{−3})	1.961
μ (mm ^{−1})	1.697
$F(000)$	1176
R_1 ($I > 2\sigma(I)$)	0.0650
wR_2 ($I > 2\sigma(I)$)	0.1480
R_1 (all data)	0.0724
wR_2 (all data)	0.1583
GOF on F^2	1.149

2.4. Theoretical Calculation Method

All density functional theory (DFT) calculations applied in this study were performed with B3LYP functional with the LANL08(f) basis set for Rh atoms and cc-pVDZ for other atoms using the Gaussian 09 (C.02) program package [39]. The geometry optimizations of $[Rh_2(O_2CCH_3)_3(PABC)]$, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, and **1D** were carried out without symmetry constraints (see Supplementary Materials Figure S1 and Tables S1–S3), and the resulting optimized structures were confirmed to be energy minima by the frequency analyses.

3. Results

3.1. Synthesis and Characterizations

Complex **1** was synthesized by the solvothermal reaction of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ and HPABC (in 1:1 molar ratio) in CH_3CN at 413 K for 6 h with a Teflon-lined steel autoclave. The pure product of **1** can be purified by silica-gel column chromatography (Eluent: 5% MeOH in CHCl_3) with a 15.9% yield. The obtained **1** is stable in air (even in moist air) and can be dissolved in DMF. Complex **1** was characterized by ^1H NMR, ESI-TOF-MS, infrared spectroscopy, and elemental analysis. In the ^1H NMR spectrum measured in $\text{DMF-}d_7$ (see Figure S2), the two doublet signals, which were assigned as aromatic protons in the PABC ligand, were detected at 7.55 and 6.54 ppm. Moreover, a singlet signal that was derived from the amino protons appeared at 5.78 ppm. The signals for methyl protons in O_2CCH_3 ligands were divided into two signals (1.71 and 1.79 ppm) with the integral intensities of 2:1, which correspond to the *cis*- and *trans*-positions, respectively, relative to the PABC ligand. As depicted in Figure S3, the ^1H NMR spectral features of **1** measured in $\text{DMSO-}d_6$ were similar to those measured in $\text{DMF-}d_7$. In the positive-ion mode ESI-TOF-MS, the signal was observed at 541.8783 m/z , which corresponds to the $[\text{M}+\text{Na}]^+$ value of complex **1** (541.8800 m/z). As depicted in Figure S4, the observed shape and pattern of the isotope pattern also fit well with the simulated isotope distribution of complex **1**. Moreover, no signal assignable to unreacted $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ was not detected. In the infrared spectrum (ATR method), the weak absorption bands of the amino group were observed at 3273 and 3184 cm^{-1} . The asymmetric $[\nu(\text{CO}_2^-)_{\text{asymm}}]$ and symmetric $[\nu(\text{CO}_2^-)_{\text{symm}}]$ vibrations of the bridging carboxylate groups were observed at 1596–1575 and 1402 cm^{-1} , respectively, which are close to those of homoleptic paddlewheel-type Rh_2 complexes such as $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ [$\nu(\text{CO}_2^-)_{\text{asymm}} = 1587 \text{ cm}^{-1}$, $\nu(\text{CO}_2^-)_{\text{symm}} = 1437 \text{ cm}^{-1}$] [36]. The vibration of the carboxylic acid group owing to the presence of the unreacted HPABC was not observed in the spectrum. The purity of complex **1** was further confirmed by CHN elemental analysis; the observed ratio of carbon, hydrogen, and nitrogen of the obtained powder was in good agreement with the calculated ratio of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$ ($\text{Rh}_2\text{C}_{13}\text{H}_{15}\text{NO}_8$), as shown in the experimental section.

3.2. Crystal Structure

Small purple-colored single crystals of **1P**, which are suitable for single-crystal X-ray diffraction analysis, can be obtained by the slow evaporation of the DMF solution of **1**. The X-ray diffraction pattern revealed that this complex crystallized in the monoclinic system with the space group $P 2_1/c$. The final refined model of **1P** is shown in Figure 2, and the crystallographic data and structural parameters of **1P** are summarized in Tables 1 and 2, respectively.

Table 2. Structural parameters of **1P** (bond length: Å, bond angle: °).

Bond Lengths					
Rh(1)-Rh(2)	2.3840(8)	Rh(2)-O(6)	2.046(5)	O(4)-C(8)	1.253(10)
Rh(1)-O(1)	2.039(5)	Rh(2)-O(8)	2.044(5)	O(5)-C(10)	1.255(9)
Rh(1)-O(3)	2.029(5)	Rh(1)-N(1)	2.293(5)	O(6)-C(10)	1.262(9)
Rh(1)-O(5)	2.032(5)	Rh(2)-O(9)	2.308(5)	O(7)-C(12)	1.255(10)
Rh(1)-O(7)	2.047(5)	O(1)-C(1)	1.263(9)	O(8)-C(12)	1.277(10)
Rh(2)-O(2)	2.033(5)	O(2)-C(1)	1.254(9)		
Rh(2)-O(4)	2.023(5)	O(3)-C(8)	1.266(10)		
Bond Angles					
Rh(1)-Rh(2)-O(2)	87.71(14)	Rh(1)-Rh(2)-O(9)	176.26(14)	O(6)-Rh(2)-O(4)	89.2(2)
Rh(1)-Rh(2)-O(4)	88.66(14)	Rh(2)-Rh(1)-N(1)	176.38(15)	O(6)-Rh(2)-O(8)	89.4(2)
Rh(1)-Rh(2)-O(6)	88.52(15)	O(1)-Rh(1)-O(3)	89.6(2)	O(1)-C(1)-O(2)	127.2(7)
Rh(1)-Rh(2)-O(8)	87.69(15)	O(1)-Rh(1)-O(7)	91.2(2)	O(3)-C(8)-O(4)	128.1(8)
Rh(2)-Rh(1)-O(1)	88.64(14)	O(5)-Rh(1)-O(3)	90.1(2)	O(5)-C(10)-O(6)	127.4(7)
Rh(2)-Rh(1)-O(3)	87.95(15)	O(5)-Rh(1)-O(7)	88.9(2)	O(7)-C(12)-O(8)	126.2(7)
Rh(2)-Rh(1)-O(5)	87.88(15)	O(2)-Rh(2)-O(4)	90.7(2)		
Rh(2)-Rh(1)-O(7)	88.79(15)	O(2)-Rh(2)-O(8)	90.4(2)		

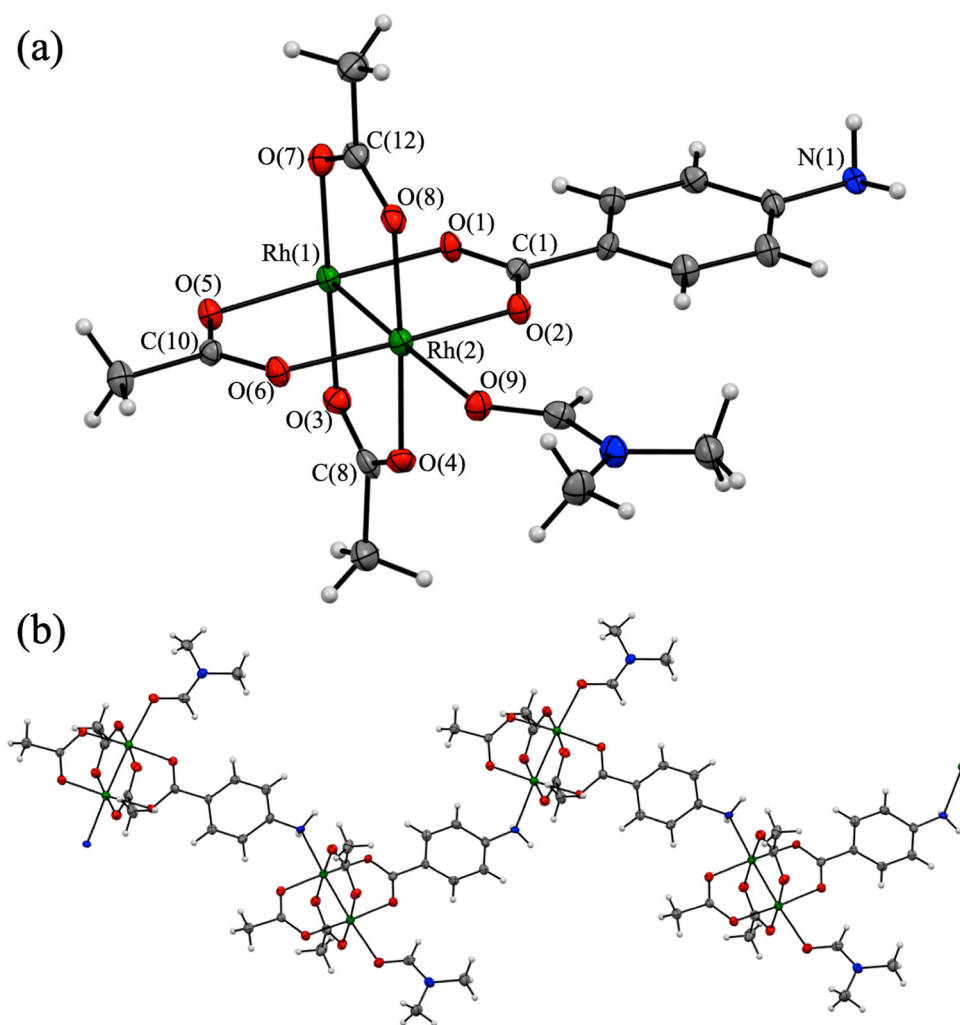


Figure 2. (a) Asymmetric unit of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]_n$ (**1P**) (30% thermal ellipsoid probability). (b) One-dimensional coordination structure of **1P** (Rh: green, O: red, N: blue, C: gray, and H: white).

The asymmetric unit of **1P** contains two Rh ions, three O_2CCH_3 ligands, one PABC ligand, and one DMF molecule (Figure 2a) and adopts a typical paddlewheel-type structure in which the Rh_2 core is coordinated by the bridging carboxylates of three O_2CCH_3 ligands and one PABC ligand at the equatorial positions. Figure 2b shows that the structural unit of **1P** was self-assembled to form the one-dimensional chain (polymeric) structure using the rhodium-amine coordination bond. Therefore, the axial position of the Rh_2 core was coordinated by one O atom of the DMF molecule and one N atom of the PABC ligand. Thus, both Rh ions in **1P** have a distorted octahedral coordination environment. The Rh-Rh bond length of **1P** is estimated as $2.3840(8) \text{ \AA}$, which is within the typical range of the Rh-Rh bond length of homoleptic paddlewheel-type Rh_2 complexes such as $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{DMF})_2]$ ($2.383 \text{ \AA}$) [40] and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NHet})_2]$ ($2.402 \text{ \AA}$) [41]. The differences in the Rh-O(carboxylate) bond lengths in **1P** are negligible and less than $0.024 \text{ \AA}$. The O-C-O angles of the bridging carboxylates of **1P** are in the range of $126.2(7)^\circ$ – $128.1(8)^\circ$, which are also close to those of the paddlewheel-type Rh_2 complex, such as $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{DMF})_2]$ (125.1° – 126.2°) [40]. However, the Rh-N(amine) and Rh-O(DMF) bond lengths in **1P** are $2.293(5)$ and $2.308(5) \text{ \AA}$, respectively, which are clearly longer than those of Rh-O(carboxylate). These results indicate that the coordination bonds in the axial sites of **1P** were weaker than those in the equatorial sites. The phenyl rings of the PABC ligand in **1P** are almost coplanar (2.87°) relative to the Rh_2 -carboxylate(PABC) plane. This result suggests the formation of

the transition dipole moment between the PABC ligand and the Rh₂ moiety [25]. As shown in Figure S5, the one-dimensional chains of **1P** were closely assembled in the crystal without non-coordinated DMF molecules.

3.3. Self-Assembly and Disassembly Phenomena

As shown in Figure 3, a green solution was obtained when **1** was dissolved in DMF, and the evaporation of DMF from the green solution produced a purple-colored crystalline product **1P**. On the basis of the color of the solution and the knowledge of previously reported paddlewheel-type Rh₂ complexes [7], it is speculated that [Rh₂(O₂CCH₃)₃(PABC)(DMF)₂] (**1D**), in which two DMF molecules are coordinated with the axial sites of Rh₂ ions, is formed in the DMF solution because the solution and solids of the paddlewheel-type Rh₂ complexes with axial *O*-donor ligands typically have a green color while those with axial *N*-donor ligands have a purple (or red) color [7]. Remarkably, we confirmed that the polymeric species **1P** can be easily re-dissolved in DMF and afford **1D**, which results in the green color of the solution. This indicates that the self-assembly and disassembly transformations between **1D** and **1P** easily occur by the dissolution and evaporation procedures with DMF.

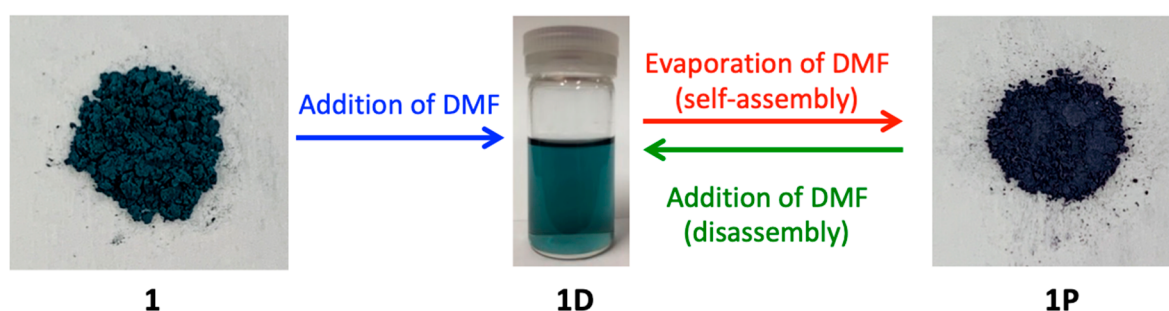


Figure 3. Pictures of **1** (green powder), **1D** in DMF (green solution), and **1P** in solid state (purple powder).

To investigate the absorption properties of **1P** and **1D**, the absorption spectrum of **1D** in DMF and the diffuse reflectance spectrum of **1P** were measured at room temperature (see Figure 4). In the visible light region, both **1D** and **1P** show two absorption maxima. The lower energy absorption band of **1P** was observed at 572 nm, which was slightly blue-shifted compared to that of **1D** (586 nm), while the higher energy absorption bands of **1D** (444 nm) and **1P** (441 nm) were located at approximately the same position. Hence, the origin of the color difference between **1D** and **1P** is primarily due to the difference in the location of their lower energy absorption bands. The other difference in the absorption bands between **1D** and **1P** was also confirmed in the UV region; **1P** shows an intense absorption band at 341 nm, which is not detected in the absorption spectrum of **1D**. Since this intense band of **1P** arises from the visible light region (~441 nm), it is confirmed that this absorption band edge slightly influences the color of **1P**. Although **1D** shows an intense absorption band at 295 nm ($\epsilon = 29,472 \text{ M}^{-1}\text{cm}^{-1}$) in the UV region, **1P** shows three continuous absorption bands at 281, 260, and 214 nm.

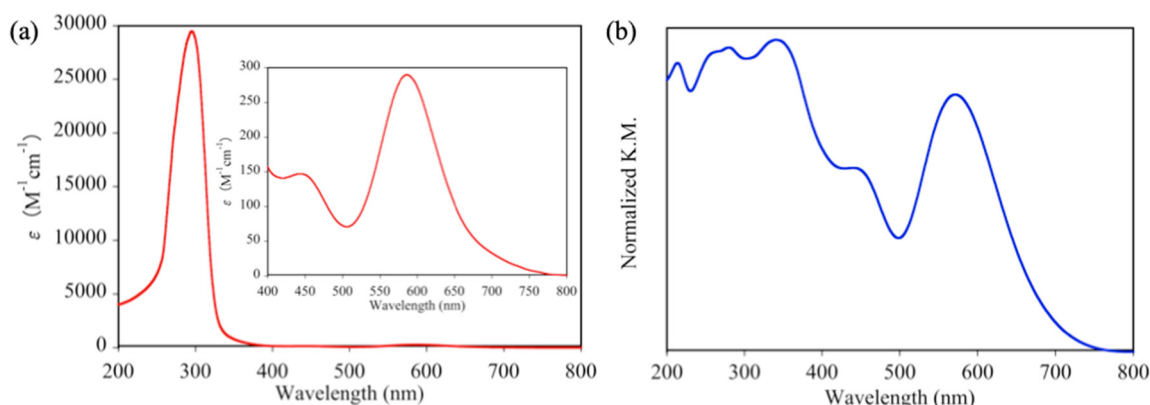


Figure 4. (a) Absorption spectrum of **1D** in DMF and (b) diffuse reflectance spectrum of **1P**.

The coordination nature of paddlewheel-type Rh_2 complexes can be easily discerned from their absorption spectra. In detail, Cotton et al. confirmed that paddlewheel-type Rh_2 complexes without axial donor ligands show an intense d-d(Rh_2) absorption band at approximately 760 nm [42]. In contrast, the absorption spectrum of **1D** shows no related band in the same region. This result indicates that two DMF molecules are coordinated at the two axial sites of Rh_2 ions of **1D**, which is similar to $[Rh_2(O_2CCH_3)_4(DMF)_2]$ [40].

To further confirm the molecular structure of **1D** in DMF, DFT calculations were performed using the model structures of **1D**, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, and $[Rh_2(O_2CCH_3)_3(PABC)]$, in which Rh_2 ions are coordinated by two, one, and no DMF molecules, respectively (their molecular structures are shown in Figure S1, and selected geometrical parameters are summarized in Table S4). The fully optimized structures of **1D**, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, and $[Rh_2(O_2CCH_3)_3(PABC)]$ commonly had paddlewheel-type structures with Rh-Rh bond lengths of 2.418, 2.407, and 2.381 Å, respectively, which is similar to the crystal structure of **1P**. As expected, the obtained sum of electronic and thermal free energy of the optimized geometry of **1D** is approximately 1.41 and 7.31 kcal/mol more stable than those of $([Rh_2(O_2CCH_3)_3(PABC)(DMF)] + DMF)$ and $([Rh_2(O_2CCH_3)_3(PABC)] + \text{two DMF})$, respectively, which indicates that **1D** should be a thermodynamically favorable species in DMF (see Table S5).

3.4. Powder X-Ray Diffraction and TG Analyses of **1P**

To investigate the phase purity and thermal stability of **1P**, powder X-ray diffraction (XRD) and TG analyses were performed. As depicted in Figure 5a, the observed XRD pattern of **1P** is in good agreement with the simulated pattern of the crystal structure of **1P**. This result indicates that the obtained **1P** has a crystalline single phase. The TG analysis of **1P** shows a distinct three-step weight loss process (see Figure 5b). The initial step in the temperature range of 27–249 °C corresponds to the loss of the DMF molecule (Obs. −12.8%, Calcd. −12.3%), which is coordinated to the axial site of Rh_2 ions in **1P**, whereas the second (249–315 °C) and third (315–700 °C) steps are attributed to the decomposition of the O_2CCH_3 and PABC ligands of **1P**, respectively. This TG result is also consistent with the chemical formula of the crystal structure of **1P**.

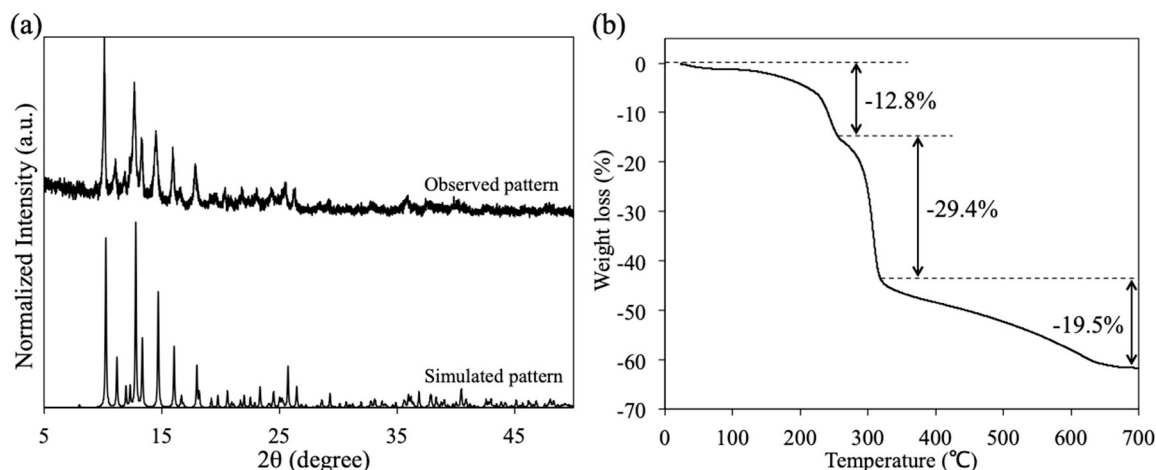


Figure 5. (a) Observed and simulated X-ray diffraction (XRD) patterns of **1P** and (b) thermo-gravimetric (TG) curve of **1P**.

4. Conclusions

In this study, we successfully developed a new synthetic strategy for CPs with heteroleptic paddlewheel-type Rh_2 -SBUs using coordination-induced self-assembly with an amino group of the PABC ligand. Single-crystal X-ray diffraction analyses clarified that **1P**, which is obtained by the slow evaporation of DMF-dissolved **1**, forms a one-dimensional polymeric structure in which two axial sites of the Rh_2 ion in **1P** are coordinated by a DMF molecule and an amino group of the PABC ligand of the neighboring molecule **1**. It is also confirmed that polymeric species **1P** can be easily re-dissolved in DMF, which indicates that the self-assembly and disassembly transformations between **1D** and **1P** easily occurred by dissolution and evaporation procedures with DMF. As previously reported, the types of organic solvents in the synthetic processes of CPs and MOFs affect their molecular and self-assembly structures [43–45]. We speculate that weak O-donor solvents are preferable in the synthetic strategy with Rh_2 -SBUs. It is expected that this synthetic strategy can be applied to the synthesis of various novel CPs with heteroleptic Rh_2 -SBUs using similar ligands with potential coordination donor sites.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/2/85/s1>, Figure S1: Optimized geometries of (a) $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$, (b) $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]$, and (c) $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})_2]$ (**1D**); Figure S2: ^1H NMR spectrum of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$ (**1**) in $\text{DMF}-d_7$; Figure S3: ^1H NMR spectrum of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$ (**1**) in $\text{DMSO}-d_6$; Figure S4: Observed (top) and simulated (down) ESI-TOF-MS spectra of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$ (**1**); Figure S5: Packing view (along an axis) of the crystal structure of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]_n$ (**1P**). Hydrogen atoms are omitted for clarity; Table S1: Coordinate of optimized geometry of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$; Table S2: Coordinate of optimized geometry of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]$; Table S3: Coordinate of optimized geometry of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})_2]$; Table S4: Selected geometrical parameters of optimized geometries of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]$, and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})_2]$ (**1D**); Table S5: Sum of electronic and thermal free energies of optimized geometries of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})]$, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})]$, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{PABC})(\text{DMF})_2]$ (**1D**), and DMF.

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