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Co-Crystallization and Structural Studies of Benzophenone Recognized by Positively Shifted ESPs of Perfluorinated β -Diketonate Complexes (M = Cu, Pd, Pt)

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Abstract: Benzophenone was encapsulated in molecular crystals of fully fluorinated coordination complexes, $[ML_2]$ [1, M = Cu^{2+} and Pd^{2+} , L = bis(pentafluorobenzoyl)-methanido[−]], forming a unique chiral co-crystal with a ratio of $[ML_2]$:benzophenone = 2:3, while no encapsulation was observed in the corresponding non-fluorinated complexes $[M(dbm)_2]$ (dbm = dibenzoylmethanido[−]). Notable π -hole $\cdots\pi$ and metal(M) $\cdots\pi$ interactions were detected between the complex and the adapted orientation of benzophenone in the co-crystals. Analyses from crystal structures and thermogravimetric (TG) results indicated that the encapsulation and thermal stability of benzophenone in these molecular crystals correlate well with the electrophilic characteristics shown by the electrostatic potential (ESP) at the metal centers, which is enhanced by fluorination: $Cu^{2+} > Pd^{2+} \gg Pt^{2+}$. The recognition of benzophenone is driven by π -holes created by the electron-withdrawing nature of fluorine atoms and the electron-deficient metal ion enhanced by the aromatic fluorine, demonstrating that the effect of electrostatic molecular recognition is as significant as oxygen coordination, as shown in comparative studies with 1,1-diphenylethylene.

Keywords: benzophenone; co-crystal; DFT calculations; fluorine effect; π -hole



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1. Introduction

Benzophenone and its derivatives are attractive guest molecules [1,2], and their reaction activities [3], nonlinear optics properties [4,5], ultraviolet absorbent characteristics [6,7], and molecular chirality [8] have been investigated as crucial materials in the fields of crystallography and host-guest chemistry [9–18]. Since benzophenone is an archetypal phosphor and exhibits fast emission in the crystalline state, its phosphorescence properties have been widely investigated, alongside the orientation of the crystal structure [19,20]. The fluorine-substituted aromatic compounds demonstrated guest encapsulations, and their unique interactions were intriguingly investigated by Gabbaï et al., who reported a trimeric tetrafluoro-ortho-phenylene mercury complex with several ketone molecules, in which the carboxylic oxygen in benzophenone coordinated with the mercury atoms through $Hg\cdots O$ μ_3 -coordination forms [2]. On the other hand, we found a unique molecular recognition and co-crystallization of an anisole molecule in the non-porous crystals of perfluorinated Cu^{2+} complexes **1a** and **2** (Figure 1) [21,22], which have pentafluorophenyl-substituted ligands. For the investigation of several fluorine-substituted complexes, two anisole molecules were encapsulated in their crystals through weak $Cu\cdots O$ interactions for **1a** and the corresponding tetrafluorophenyl-substituted complex, but no remarkable $Cu\cdots O$ interactions were observed in the corresponding trifluorophenyl-substituted complex, and no encapsulations were observed in di- and mono-fluorophenyl-substituted complexes [21]. The driving forces of encapsulation phenomena of aromatic compounds in the crystals of perfluorinated complexes are considered to be π -hole $\cdots\pi$ interactions [23–27], provided by the positive quadrupole moment [28–30] of fully fluorinated aromatic rings, and metal $\cdots\pi$

interactions [31–33], provided by the cationic nature induced by metal ions. However, guest encapsulations always depend on the size compatibility between the host and guest molecules. Therefore, this study investigated whether the metal complex of **1a**, which contains pentafluorophenyl groups, can encapsulate benzophenone, a guest molecule larger than the metal center of the complex.

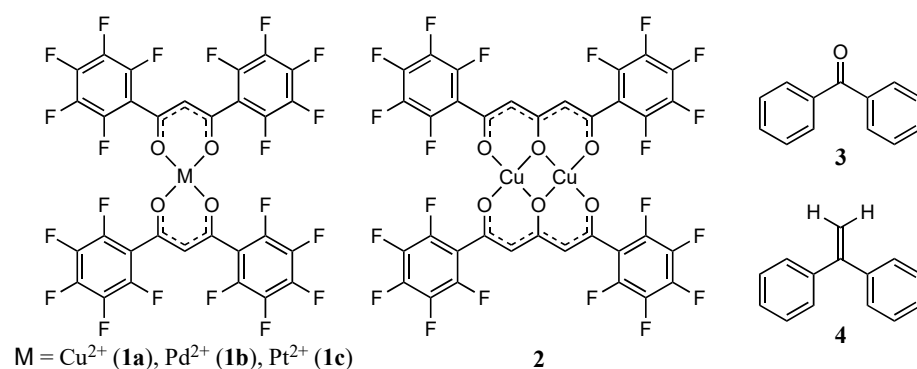


Figure 1. Molecular structures of **1–4**.

Based on the research, we were prompted to investigate the crystallization of fully fluorinated complex **1a** and benzophenone **3** to understand the size affinity and release characteristics of dispersed benzophenone **3** in molecular crystalline states because the luminescence is sensitive to changes in the local atomic configuration of the crystal structures [34]. Herein, we report co-crystallizations of **1** and **3**, depending on the metal centers of fully fluorinated complexes **1a** (M = Cu²⁺), **1b** (M = Pd²⁺), and **1c** (M = Pt²⁺) [35,36], which were selected as square-planar metal ions with open coordination axes, based on crystallographic and thermogravimetric (TG) studies. During the investigation, we also discovered the electrophilic properties and the positive electrostatic potentials (ESPs) on the surfaces of Cu²⁺ and Pd²⁺ in the complexes, which were significantly induced and enhanced by fluorination to facilitate molecular recognition of **3** in the crystalline states. On the other hand, fluorination does not significantly impair the strong nucleophilic properties of the Pt²⁺ center of **1c**. Consequently, we found that the molecular recognition behavior of nucleophilic **1c** is not well-suited for benzophenone, in contrast to the behavior exhibited by the two electrophilic complexes, **1a** and **1b**. To further understand the guest recognition induced by fluorination of metal complexes, we investigated the co-crystallization involving a dinuclear complex (**2**) with enhanced charge at the metal centers as hosts, and 1,1-diphenylethylene **4** as a guest, which allows for the exclusion of the carbonyl oxygen coordination of **3**.

2. Materials and Methods

2.1. General

Complexes **1** and **2** [21,22,35,36] were prepared using previously reported protocols with their corresponding ligands [37]. Benzophenone (BP, **3**), 1,1-diphenylethylene (DPE, **4**), and solvents were of reagent grade and were used without further purification. The TG analysis was performed using a TA TGA-Q500 (TA Instruments, Tokyo, Japan). The ESP was calculated by DFT using the Spartan'20 package (V1.1.4) with ω B97X-D/6-31G* (Wavefunction Inc., Tokyo, Japan).

2.2. Crystal Structure Determination

Single crystals suitable for X-ray crystallographic studies were obtained through the natural evaporation of a CHCl₃ (or CH₂Cl₂) solution of each complex, **1** or **2**, with guests, **3** or **4**. The crystal structures were determined by a Bruker D8 QUEST diffractometer with a graphite monochromator and MoK α radiation ($\lambda = 0.71073$ Å) generated at 50 kV and 1 mA. Crystals were coated with paratone-N oil and measured during 100–150 K. The SHELXT

program was used to solve the structures [38]. Refinement and further calculations were carried out using SHELXL [39]. The crystal data and structure refinements are summarized in Table 1 for three isomorphs of $(1)_2 \bullet (3)_3$ and in Table 2 for the corresponding structures of $2 \bullet (3)_2$, $2 \bullet (3)_4$, $1a \bullet (4)_{1.5}$, and $2 \bullet (4)_2$. All H atoms were placed in geometrically idealized positions and refined as riding, with aromatic C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Table 1. Crystal data and structure refinement for $(1)_2 \bullet (3)_3$.

	$(1a)_2 \bullet (3)_3$	$(1b)_2 \bullet (3)_3$	$(1c)_2 \bullet (3)_3$
Description	Prismatic	Prismatic	Prismatic
Chemical formula	$\text{C}_{99}\text{H}_{34}\text{Cu}_2\text{F}_{40}\text{O}_{11}$	$\text{C}_{99}\text{H}_{34}\text{F}_{40}\text{O}_{11}\text{Pd}_2$	$\text{C}_{99}\text{H}_{34}\text{F}_{40}\text{O}_{11}\text{Pt}_2$
Formula weight	2286.34	2372.06	2549.44
Temperature [K]	103	103	123
Crystal system	monoclinic	Monoclinic	monoclinic
Space group	Cc	Cc	Cc
<i>a</i> [Å]	31.4023(17)	31.269(2)	31.354(5)
<i>b</i> [Å]	15.0085(7)	15.1818(10)	15.220(3)
<i>c</i> [Å]	24.0330(12)	24.045(3)	24.470(4)
β [°]	129.932(1)	130.098(2)	130.441(4)
<i>V</i> [Å ³]	8685.5(8)	8731.5(13)	8887(3)
<i>Z</i>	4	4	4
<i>D_c</i> [Mg m ^{−3}]	1.748	1.804	1.905
μ [mm ^{−1}]	0.642	0.563	3.294
<i>F</i> (000)	4536	4672	4928
<i>R</i> _{int}	0.1012	0.1071	0.0264
GOF	1.033	1.172	1.016
<i>R</i> [(<i>I</i>) > 2σ(<i>I</i>)]	0.0345	0.0712	0.0164
<i>wR</i> (<i>F</i> _o ²)	0.0724	0.1298	0.0355
Flack parameter	0.271 (8)	0.47 (4)	0.214 (3)
CCDC No.	1901579	1901580	2361541

Table 2. Crystal data and structure refinement for copper complexes with 3 and 4.

	$2 \bullet (3)_2$	$2 \bullet (3)_4$	$1a \bullet (4)_{1.5}$	$2 \bullet (4)_2$
Description	Plate	Prismatic	Block	Block
Chemical formula	$\text{C}_{60}\text{H}_{24}\text{Cu}_2\text{F}_{20}\text{O}_8$	$\text{C}_{43}\text{H}_{22}\text{CuF}_{10}\text{O}_5$	$\text{C}_{51}\text{H}_{15}\text{CuF}_{20}\text{O}_4$	$\text{C}_{62}\text{H}_{28}\text{Cu}_2\text{F}_{20}\text{O}_6$
Formula weight	1379.87	872.14	1135.17	1375.92
Temperature [K]	100	150	100	100
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	17.900(2)	11.6773(8)	31.426(6)	17.8048(17)
<i>b</i> [Å]	8.0289(9)	13.0175(9)	15.545(3)	8.1625(8)
<i>c</i> [Å]	18.0922(18)	14.2065(9)	23.673(5)	17.9524(18)
α [°]	90	63.385(2)	90	90
β [°]	92.686(3)	84.163(2)	129.866(4)	93.253(3)
γ [°]	90	69.029(2)	90	90
<i>V</i> [Å ³]	2597.3(5)	1798.4(2)	8877(3)	2604.8(4)
<i>Z</i>	2	2	8	2
<i>D_c</i> [Mg m ^{−3}]	1.764	1.611	1.699	1.754
μ [mm ^{−1}]	0.951	0.708	0.625	0.946
<i>F</i> (000)	1372	878	4496	1372
<i>R</i> _{int}	0.1815	0.0508	0.0674	0.3277
GOF	1.204	0.918	1.094	0.815
<i>R</i> [(<i>I</i>) > 2σ(<i>I</i>)]	0.0973	0.0429	0.0483	0.0339
<i>wR</i> (<i>F</i> _o ²)	0.2018	0.1438	0.1266	0.0658
CCDC No.	2361542	2361543	2361544	2361545

3. Results and Discussion

3.1. Preparation and Thermogravimetric Analysis of Co-Crystals

Co-crystals were obtained from the natural evaporation of a CHCl_3 (or CH_2Cl_2) solution of each complex with the guest molecule. Typically, complex **1a** and benzophenone **3** were dissolved in CHCl_3 , and the solution was slowly evaporated using a pin-hole to yield deep green crystals, $(\mathbf{1a})_2 \bullet (\mathbf{3})_3$. The crystals were precipitated quantitatively by concentrating the solution. While it is not possible to distinguish between the crystals of the guest-free and guest-included complexes by appearance, the guest-included complex crystals can be differentiated from the guest, such as the colorless benzophenone, making it preferable for the stoichiometric ratio of the host to the guest to be either equal or have an excess of the guest. Final encapsulation numbers were characterized by TG and single-crystal X-ray structure analysis, indicating the formation of $(\mathbf{1})_2 \bullet (\mathbf{3})_3$ as isomorphs for **1a** and **1b**. Unfortunately, uniform crystallization of **1c** and **2** could not be found; brown prismatic microcrystals with no guest encapsulated in **1c** were more frequently obtained than the orange block crystal of $(\mathbf{1c})_2 \bullet (\mathbf{3})_3$. Meanwhile, crystals $(\mathbf{1a})_2 \bullet (\mathbf{3})_3$ and $(\mathbf{1b})_2 \bullet (\mathbf{3})_3$ were quantitatively obtained under several conditions, as characterized by the appearance and TG analysis. Co-crystallizations of **2** with **3** and **4** were performed using the same protocols as for **1**, and the detailed characterization was discussed in the crystallographic studies. Additionally, the co-crystallization with these complexes allows for the differentiation of the crystals by the quenching of the characteristic luminescence of **3**.

To understand the quantitative amounts of guest encapsulations and the thermal stabilities of the intermolecular interactions, the results of the TG analysis are shown in Figure 2. As a result, the total elimination of the guest molecules showed good agreement with the X-ray crystallographic results. In the crystal of $(\mathbf{1a})_2 \bullet (\mathbf{3})_3$, the elimination process slowly started at 110 °C, and the total elimination of benzophenone was observed to be −22.9% from 110 to 180 °C, which was close to the calculated value of −23.9%, indicating that 1.46 equivalents (the stoichiometry of **1a**:**3** is 2:3) of benzophenone molecules were included in the crystal of Cu^{2+} complex **1a**. In the crystal of $(\mathbf{1b})_2 \bullet (\mathbf{3})_3$, the elimination process slowly started at room temperature (r.t.), and the weight loss occurred mainly between 100 and 150 °C. The total elimination of **3** was observed to be −22.3% from r.t. to 150 °C, which was also close to the calculated value of −23.0%. On the other hand, the crystals prepared from the Pt^{2+} complex **1c** and **3** in a CHCl_3 solution showed no mass reduction, indicating minimal guest encapsulation and stabilization of $(\mathbf{1c})_2 \bullet (\mathbf{3})_3$. These results show that the strength of intermolecular interactions and thermal stability between complex **1** and benzophenone **3** varied significantly with the central metals: **1a** > **1b** (>>**1c**).

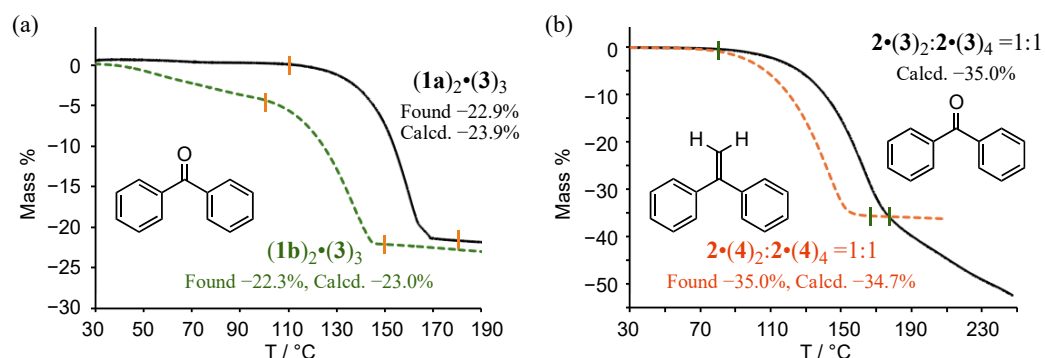


Figure 2. TG curves of (a) $(\mathbf{1a})_2 \bullet (\mathbf{3})_3$ (black, solid) and $(\mathbf{1b})_2 \bullet (\mathbf{3})_3$ (green, dashed) and (b) $2 \bullet (\mathbf{3})_n$ (black, solid) and $2 \bullet (\mathbf{4})_n$ (orange, dashed). The scan rate was 5.0 °C min^{−1}.

On the other hand, the results using the dinuclear complex **2** showed retention of guest molecules up to approximately 80 °C, followed by a release process; the first-step of elimination of **3** was observed to be around −35% from 80 to 180 °C, while the total elimination of **4** was observed to be −35.0% from 80 to 170 °C. These experiments

were performed using crystals rather than powders, and the results indicated that three guest molecules were incorporated per complex **2**. This reduction suggests not uniform recognition of three molecules per complex to estimate $2\bullet(3)_3$ and $2\bullet(4)_3$, but rather the formation of pseudopolymorphic crystals incorporating two and four guest molecules, i.e., 1:1 mixture of $2\bullet(3)_2:2\bullet(3)_4$ and $2\bullet(4)_2:2\bullet(4)_4$ as will be discussed in the following crystallographic studies.

3.2. Crystal Structure of $(1a)_2\bullet(3)_3$

An asymmetric unit of $(1a)_2\bullet(3)_3$ is shown in Figure 3. The crystal of $(1a)_2\bullet(3)_3$ comprises the entire structures of two complexes, **1a**, and three benzophenones, **3**, to form a monoclinic *Cc* based on the chiral orientation of the central benzophenone (*BP-3*) in the crystals. For the depiction of the crystal structure, two types of **1a** and three types of **3** are denoted as *C-1*, *C-2*, *BP-1*, *BP-2*, and *BP-3*, respectively. Typically, in $(1a)_2\bullet(3)_3$, the two complexes, *C-1* and *C-2*, are crystallographically non-equivalent but structurally in the same environment. Two benzophenone molecules, *BP-1* [(*P,P*)-form] and *BP-2* [(*M,M*)-form] [8], are also in the same environments, and one phenyl group of **3** interacts with the pentafluorophenyl group of the complex through π -hole $\cdots\pi$ interactions [23,40–47] and further interacts with the metal ion of the complex located nearby through $M\cdots\pi$ interactions [21,22,31–33]. The intermolecular distance between the centroid (C_g) of one phenyl group of *BP-1* and the centroid of Ring-1 of *C-1* is 3.579(3) Å, and the interplanar distance is 3.4 Å. The detailed distances of intermolecular interactions were summarized in Table 3. On the other hand, one phenyl group of *BP-3* [(*M,M*)-form] interacts with two metal ions through $M\cdots\pi$ interactions to form a sandwich structure (Figure 3b). Another phenyl group interacts with Ring-2 of *C-1* through π -hole $\cdots\pi$ interaction, and the distance between the two centroids of the aromatic rings is 3.721(4) Å. All carbonyl oxygens of **3** show no interaction with metal centers, and the $M\cdots\pi$ and π -hole $\cdots\pi$ interactions between the aromatic rings are the only dominant interactions.

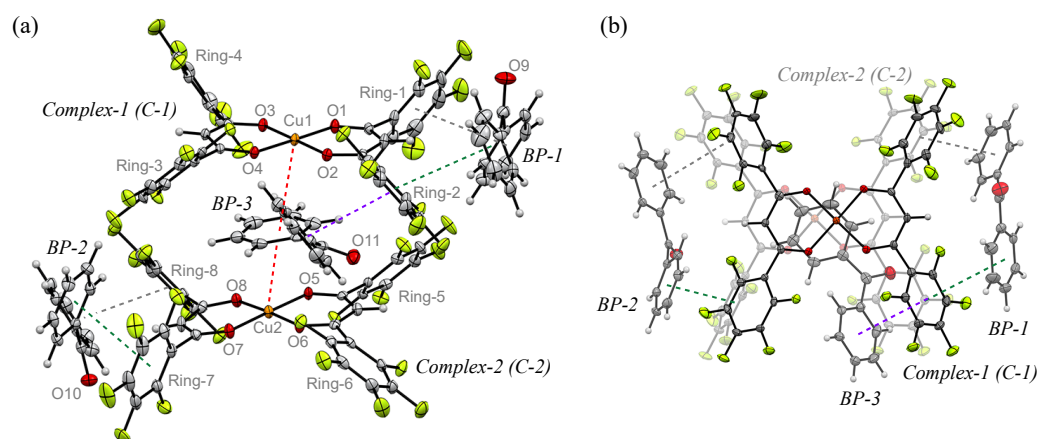


Figure 3. (a) Side and (b) top views of asymmetric unit of $(1a)_2\bullet(3)_3$ at 100 K, showing the atom-labeling schemes. Displacement ellipsoids are drawn at the 50% probability level. The red dotted lines indicate $M\cdots\pi$ interactions; the other dotted lines represent π -hole $\cdots\pi$ interactions.

A part of the packing structure of $(1a)_2\bullet(3)_3$ is shown in Figure 4. The supramolecular association of the asymmetric units is shown in Figure 4a, indicating the remarkable π -hole $\cdots\pi$ and $M\cdots\pi$ interactions. The views of independent packings of **1a**, **3**, and the whole packing structure of $(1a)_2\bullet(3)_3$ are shown in Figures 4b, 4c, and 4d, respectively. The complex **1a** forms zig-zag arrangements along the *c*-axis, and the benzophenone molecules, *BP-1* and *BP-2*, are shown in orange, and *BP-3* is shown in green, forming alternate columnar stacking along the *c*-axis. Finally, the crystal packing shows that the benzophenone **3** is dispersed and closely interacts with surrounding perfluorinated

complexes, and no remarkable intermolecular $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ interactions [48,49] were also observed between the phenyl groups of **3**.

Table 3. The distances [Å] of remarkable intermolecular interactions between the centroid of phenyl group of each *BP*-1-3 (**3**) and the centroid of pentafluorophenyl ring of **1**.

	(1a) ₂ •(3) ₃	(1b) ₂ •(3) ₃	(1c) ₂ •(3) ₃
Ph in <i>BP</i> -1 ... Ring-1	3.579(3)	4.073(12)	3.988(5)
Ph in <i>BP</i> -1 ... Ring-2	4.108(4)	3.542(9)	3.633(3)
Ph in <i>BP</i> -2 ... Ring-7	3.653(3)	3.887(12)	3.554(4)
Ph in <i>BP</i> -2 ... Ring-8	3.896(4)	3.601(8)	3.788(4)
Ph in <i>BP</i> -3 ... Ring-2 [a]	3.721(4)	3.728(11)	3.989(5)
Ph in <i>BP</i> -3 ... M1	3.389	3.437	3.583
Ph in <i>BP</i> -3 ... M2	3.436	3.492	3.524
Ph in <i>BP</i> -1 ... M2 [b]	3.524	3.521	3.523
Ph in <i>BP</i> -2 ... M1 [b]	3.401	3.435	3.575

[a] The Ph group in *BP*-3 interacts with Ring-1 for (**1b**)₂•(**3**)₃ because of the opposite molecular chirality. [b] The metal is located by symmetric operations.

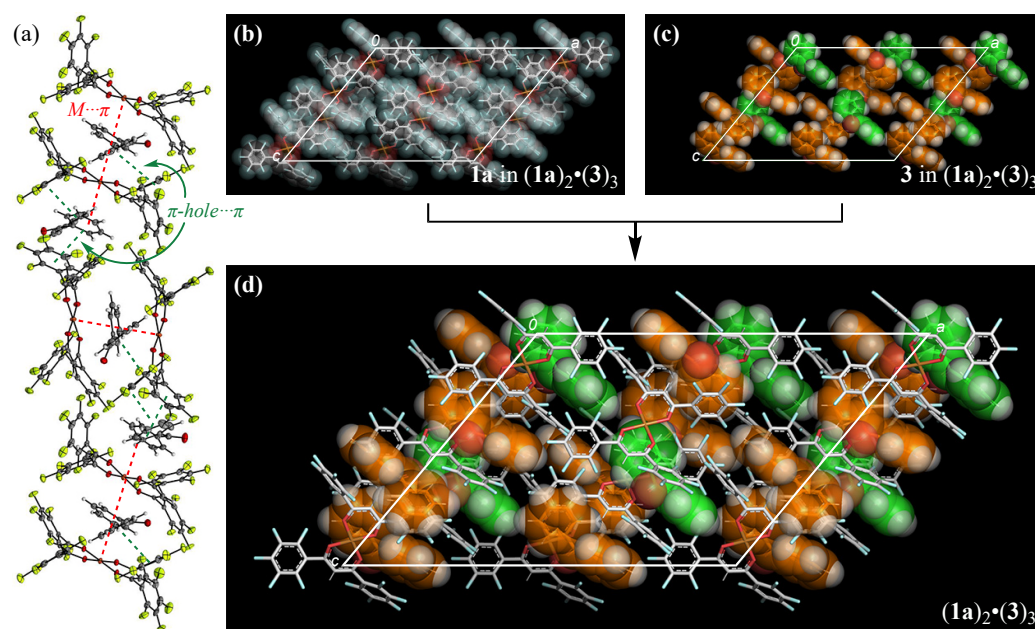


Figure 4. Crystal structures of (**1a**)₂•(**3**)₃ at 100 K: (a) supramolecular association and the parts of packings of (b) complex **1a**, (c) benzophenone **3** (*BP*-1 and *BP*-2: orange, *BP*-3: green), and (d) a whole structure of (**1a**)₂•(**3**)₃. The red and green dotted lines indicate $\text{M}\cdots\pi$ and $\pi\text{-hole}\cdots\pi$ interactions, respectively.

The crystal structures of (**1b**)₂•(**3**)₃ and (**1c**)₂•(**3**)₃ are isomorphs, and the detailed distances are shown in Table 3. The dispersion in the crystal states and the weak intermolecular interactions of **3** surrounded by **1** differ from the original crystal structures of **3** [8] and the corresponding orientation in other porous systems. The dihedral angles of the two phenyl rings in the three benzophenones in (**1a**)₂•(**3**)₃ indicate the flexible packing; they are 55.26°, 58.93°, and 60.77° for *BP*-1, *BP*-2, and *BP*-3, respectively [the corresponding angles for (**1b**)₂•(**3**)₃ are 55.26°, 58.52°, 56.66°, and for (**1c**)₂•(**3**)₃ they are 55.07°, 58.21°, 56.78°]. The dihedral angle of the chiral crystal of (*M,M*)-benzophenone (CCDC1453975) [7] is 53.87° and that of the optimized structure by DFT is 52.43°, which are close to the previously reported angle (the RMS deviation is 0.0322 Å) [10,50]. The slightly larger dihedral angle of *BP*-3 in (**1a**)₂•(**3**)₃ shows the unique environment of benzophenone sandwiched by the complexes through $\text{M}\cdots\pi$ interactions. The torsion angles between the carbonyl and phenyl group (O-C-C-C) are −27.0(2)° and −26.4(2)° for (*M,M*)-benzophenone, 26.5(8)°

and $31.7(8)^\circ$ for BP-1, $-18.2(7)^\circ$ and $-40.0(7)^\circ$ for BP-2, and $-28.2(7)^\circ$ and $-32.4(7)^\circ$ for BP-3, showing that BP-2 is also flexibly twisted for π -hole $\cdots\pi$ interactions. A structural overlay of BPs-1-3 in $(\mathbf{1a})_2\bullet(\mathbf{3})_3$ with the independent crystals is shown in Figure 5; the left sides of the $\text{C}_6\text{F}_5\text{CO}$ moieties are overlaid, showing the corresponding RMS deviations and the dihedral angles of the two phenyl rings to illustrate the structural distortion. The full molecular overlay of two structures, BP-1 and (*P,P*)-benzophenone (CCDC1453976) [8], indicates an RMS deviation of only 0.0538 Å and a maximum deviation of only 0.0758 Å. However, the RMS and maximum deviations are 0.1422 Å and 0.2460 Å, respectively, for BP-2 and (*M,M*)-benzophenone and 0.0775 Å and 0.1409 Å, respectively, for BP-3 and (*M,M*)-benzophenone, showing the good affinity of benzophenone molecules for the host frameworks. In addition to the orientation of benzophenone within the crystals, the distances involved in the $\text{M}\cdots\pi$ interactions are also noteworthy. The average $\text{M}\cdots\pi$ distances for BP-3, sandwiched between two metal complexes, are 3.41 Å for Cu, 3.46 Å for Pd, and 3.55 Å for Pt, increasing in sequence. These experimental results are intriguing, even considering the differences in atomic radii of the metal ions. Furthermore, these findings correlate well with the experimental thermal stability observed in crystallization and TG analysis, indicated by the stability sequence ($\text{Cu} > \text{Pd} \gg \text{Pt}$).

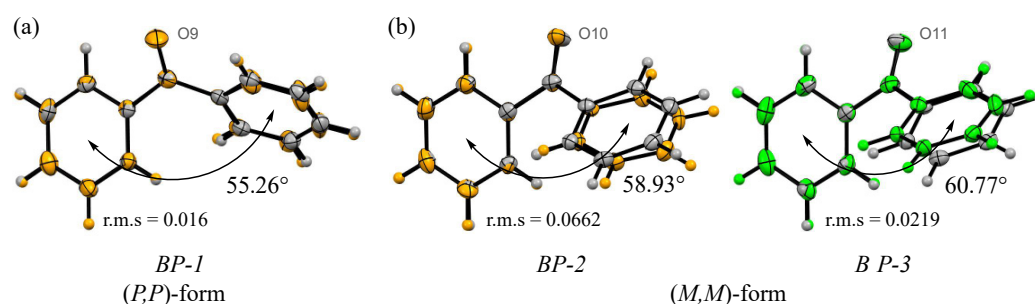


Figure 5. Structure overlay of (a) BP-1 of (*P,P*)-form and (b) BP-2 and BP-3 of (*M,M*)-form in $(\mathbf{1a})_2\bullet(\mathbf{3})_3$ with the corresponding independent crystal [7] at 100 K (BP-1 and BP-2: orange, BP-3: green, original chiral crystals of benzophenone: gray). Each left side of $\text{C}_6\text{F}_5\text{CO}$ moieties are overlaid and the corresponding r.m.s deviations are shown.

3.3. Density Functional Theory Calculations of the Structures

For understanding the intermolecular associations exerted by metal ions, DFT calculations based on the crystal structure of **1** and **2** were performed to give the electrostatic potential (ESP) surfaces, where the blue and red colors indicate electron poor and rich surface regions, respectively (Figure 6 and Table 4). The Cu, H, and the center parts of the pentafluorophenyl rings show the positive potential energy (shown as blue), while the Pt, F, and O atoms show the negative potential energy (shown as yellow-red). In contrast, the similar type of bis[dinaphthoylemethanido] $\text{M}(\text{II})$ ($\text{M} = \text{Cu}, \text{Pd}, \text{Pt}$) shows that the ESPs on metal surface are $+122.84 \text{ kJ mol}^{-1}$ for Cu^{2+} , -75 kJ mol^{-1} for Pd^{2+} , and $-113.9 \text{ kJ mol}^{-1}$ for Pt^{2+} [51], and the complex **1** using the guest-free single crystal data [21,22,52] shows the high and enhanced positive shift by the fluorination (Figure 6a); the corresponding ESPs are $+201.1 \text{ kJ mol}^{-1}$ for Cu^{2+} (**1a**), $+1.1 \sim +11.0 \text{ kJ mol}^{-1}$ for Pd^{2+} (**1b**), and $-38.5 \sim -43.0 \text{ kJ mol}^{-1}$ for Pt^{2+} (**1c**). This interesting positive shift is influenced by the twist angles of the pentafluorophenyl groups in the complex and takes a value varying in the range of about 20 kJ mol^{-1} for Pd^{2+} ; i.e., $+6.0 \sim +9.2 \text{ kJ mol}^{-1}$ and $+16.6 \sim +19.8 \text{ kJ mol}^{-1}$ for Pd^{2+} of **1b** in the crystals of $(\mathbf{1b})_2\bullet(\mathbf{3})_3$ and $\mathbf{1b}\bullet(\text{C}_6\text{H}_6)_3$ [21], respectively. The inclusion of this range in ESPs reflects the different values of front and back potentials of the complexes, and the results provide qualitative information about the surface electron distributions. The highest ESP values in the center of the pentafluorophenyl rings are $+100.2 \text{ kJ mol}^{-1}$ for **1a**, $+100.9 \text{ kJ mol}^{-1}$ for **1b**, and $+110.0 \text{ kJ mol}^{-1}$ for **1c**, which are almost the same, indicating that the co-crystallization and stabilization of benzophenone are not solely induced by the pentafluorophenyl rings but also the metal characteristics. The change in

the ESP resulting from increasing the number of Cu^{2+} from mononuclear to dinuclear is characterized by an increase in the positive charge at the copper centers and the provision of two positively charged spots at the nuclear core sites. The lowest ESP value of two phenyl rings of **3** is $-70.7 \text{ kJ mol}^{-1}$ (Figure 6c), and the whole region of ESP of **3** is from -182.29 to $+96.27 \text{ kJ mol}^{-1}$. Since the $\text{M}\cdots\pi$ interaction works between the positive electron-deficient metal and the negative aromatic π -electron, it is well explained that the co-crystals $(\mathbf{1})_2\bullet(\mathbf{3})_3$ can be formed with positive ESP on metal of **1a** and **1b** [53,54]. The ESP on metals also dominates the stability of TGA and the difficulty of co-crystallization of the Pt complex (**1c**). The lowest ESP values of two phenyl rings and the ethynyl linker of **4** are -92.0 and $-78.2 \text{ kJ mol}^{-1}$, respectively, highlighting the potential for $\text{M}\cdots\pi$ interaction with the complexes.

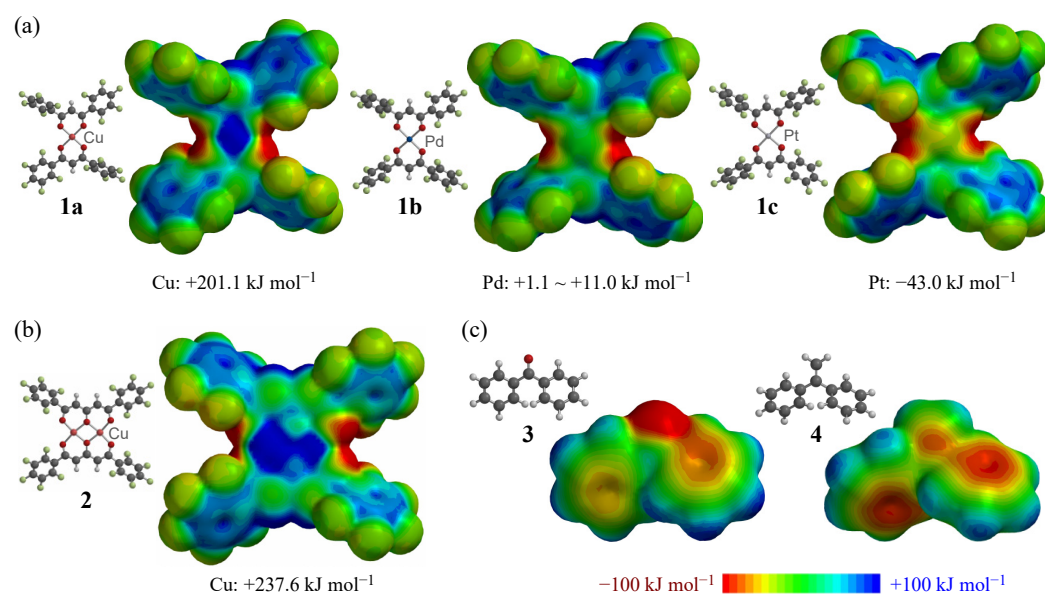


Figure 6. The energy potential maps of (a) **1** and (b) **2** from the crystal structures and (c) **3** and **4** from the optimized structures: the color of the potential is shown between -100 kJ mol^{-1} (red) to $+100 \text{ kJ mol}^{-1}$ (blue).

Table 4. The remarkable values of electrostatic potential (kJ mol^{-1}) in the compounds **1–4**.

	1a	1b	1c	2	3	4
maximum	+201.13	+137.45	+140.24	+237.56	+96.27	+77.16
minimum	−152.09	−139.14	−134.34	−148.95	−182.29	−92.03
C_g of metal	+201.1	+11.0	−38.5	+237.56	---	---
	$\sim +200.3$	$\sim +1.1$	~ -43.0	$\sim +160.3$		
C_g of aromatic ring	+100.2	+100.9	+110.0	+99.7	−70.7	−92.0
	$\sim +82.0$	$\sim +81.0$	$\sim +83.0$	$\sim +93.1$	~ -56.6	~ -90.7
others	---	---	---	---	−182.29	−78.2
					O in CO	C_g in C=C

3.4. Pseudo-Polymorph Structures of $2\bullet(\mathbf{3})_2$ and $2\bullet(\mathbf{3})_4$

The complex **1a** yielded intriguing crystals incorporating **3**, with theoretical calculations predicting coordination of oxygen at the electron-deficient axial sites of Cu^{2+} . However, in practice, an aromatic moiety of **3** closely interacted with the Cu center, predominantly influencing $\text{M}\cdots\pi$ interactions. To clarify whether this was merely due to steric hindrance influenced by the pentafluorophenyl groups of the ligand forming a hydrophobic coordination pocket, we attempted crystallization from CHCl_3 solution using a dinuclear complex **2**. The crystals grew densely at the bottom of the container and were likely co-precipitated with colorless benzophenone crystals; therefore, the crystal surface was

cleaned with a small amount of solvents or oils before the measurements. To the best of our knowledge, two types of single crystals, $2 \bullet (3)_2$ and $2 \bullet (3)_4$, were obtained as pseudopolymorphs, which are difficult to separate based on their appearances. The structure of $2 \bullet (3)_2$ is shown in Figure 7a. An asymmetric unit of $2 \bullet (3)_2$ comprises half of **2** and the entirety of **3** to give a 1:2 stoichiometry as the centrosymmetric structure. For *BP-1*, the oxygen atom O4 in **3** coordinates to Cu1 [the distance of O4...Cu1 is 2.473(7) Å] and the phenyl group shows $M \cdots \pi$ interactions [the intermolecular distance between the centroid (C_g) of one phenyl group of *BP-1* and the Cu atom is 3.399 Å]. On the other hand, an asymmetric unit of $2 \bullet (3)_4$ comprises half of **2** and the two entireties of **3**, non-coordinated *BP-1* and coordinated *BP-2*, to give a 1:4 stoichiometry as the centrosymmetric structure (Figure 7b). The oxygen atom O5 in *BP-2* coordinates to Cu1 [the distance of O5...Cu1 is 2.502(3) Å] and the phenyl group shows $M \cdots \pi$ interactions [the intermolecular distance between the centroid (C_g) of one phenyl group of *BP-2* and the Cu atom is 3.384 Å]. Structure overlays of the two benzophenone coordinated complex in the crystals of $2 \bullet (3)_2$ and $2 \bullet (3)_4$ are shown in yellow and purple, respectively (Figure 7c); both coordination sites of Cu_2O_6 moieties are closely overlapped and the corresponding RMS deviation is 0.0201.

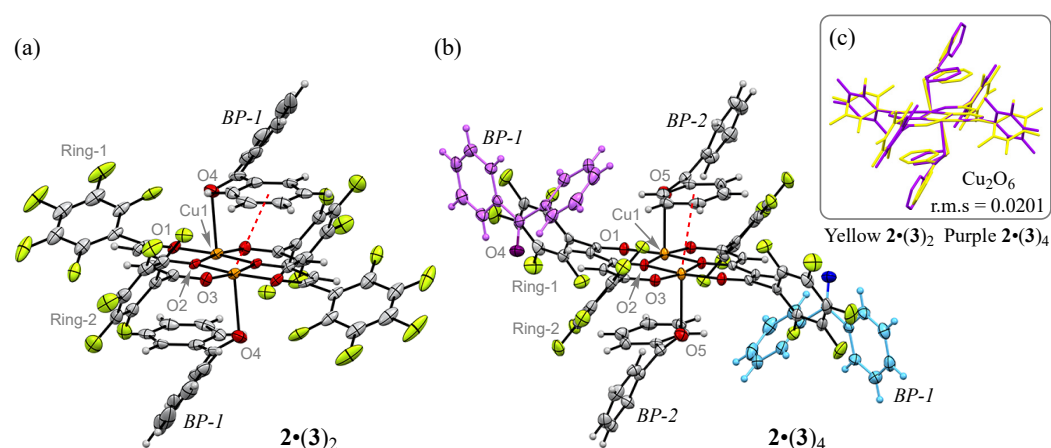


Figure 7. Crystal structures of (a) $2 \bullet (3)_2$ and (b) $2 \bullet (3)_4$, showing the atom-labeling schemes. Displacement ellipsoids of $2 \bullet (3)_2$ and $2 \bullet (3)_4$ are drawn at the 40% and 50% probability levels, respectively. The red dotted lines indicate $M \cdots \pi$ interactions. (c) Structure overlay of benzophenone coordinated complex in the crystals of $2 \bullet (3)_2$ in yellow and $2 \bullet (3)_4$ in purple, whose Cu_2O_6 moieties are overlapped, and the corresponding RMS deviation is shown.

3.5. Crystal Structure with 4

Finally, we attempted co-crystallization with a similar structure that excluded the influence of oxygen; compound **4** (DPE, 1,1-diphenylethylene) does not have a locally electron-rich region like **3**, and it is thought that only the negative charge distribution of the π electron system affects the crystal formation. Although the exact value of the crystal composition could not be obtained from TGA, crystal structure analysis revealed that mononuclear complex **1a** contains one half of molecules of **4** and also dinuclear complex **2** contains two molecules of **4** to yield $1a \bullet (4)_{1.5}$ and $2 \bullet (4)_2$, respectively.

An asymmetric unit of $1a \bullet (4)_{1.5}$ is shown in Figure 8a,b. The crystal comprises the entire structure of **1a**, one DPE-1 ($C_{14}H_{12}$), and a half of the disordered structure of DPE-2 ($C_{14}H_2$). Unfortunately, DPE-2 was not fully characterized in quantitative amount because of the symmetrically disordered arrangements. The two phenyl rings of DPE-1 show remarkable intermolecular electrostatic interactions with the π -hole; the intermolecular distance is 3.731 Å for $C_g < \text{Ring-1} > \cdots C_g < \text{Ring-5} >$, and enhanced cationic Cu, with the intermolecular distance being 3.445 Å for $Cu \cdots C_g < \text{Ring-6} >$, indicating similar environments to the corresponding benzophenone. The phenyl group of DPE-2 interacts with Cu through $M \cdots \pi$ interactions, and the corresponding shortest intermolecular distance is 3.348 Å. Apart from the characteristics of disorder in the arrangement of DPE-2, the packing structure

and intermolecular interactions within the crystal of $1\mathbf{a}\bullet(4)_{1.5}$ were very similar to those in $(1\mathbf{a})_2\bullet(3)_3$. Therefore, the unique co-crystals of $(1)_2\bullet(3)_3$ are not primarily encapsulated by the carbonyl oxygen of 3 , but rather first by the π -hole interactions of the fluorinated complexes, and the stability of the co-crystals is determined by the $M\cdots\pi$ interactions. The structure of $2\bullet(4)_2$, which comprises the half structure of $1\mathbf{a}$ and the entirety of *DPE-1*, also shows good affinity and remarkable $M\cdots\pi$ interactions between metal sites in 2 and the phenyl- and ethynyl-moieties of 4 , as shown in Figure 8c. The intermolecular distances are 3.395 Å for $\text{Cu}\cdots\text{C}_g$ <Ring-4> and 3.059 Å for $\text{Cu}\cdots\text{C}_g$ <C=C bond>. Another phenyl group of *DPE-1* further interacts with the pentafluorophenyl rings of 2 through a weak π -hole $\cdots\pi$ interaction, and the corresponding intermolecular distance is 3.990 Å.

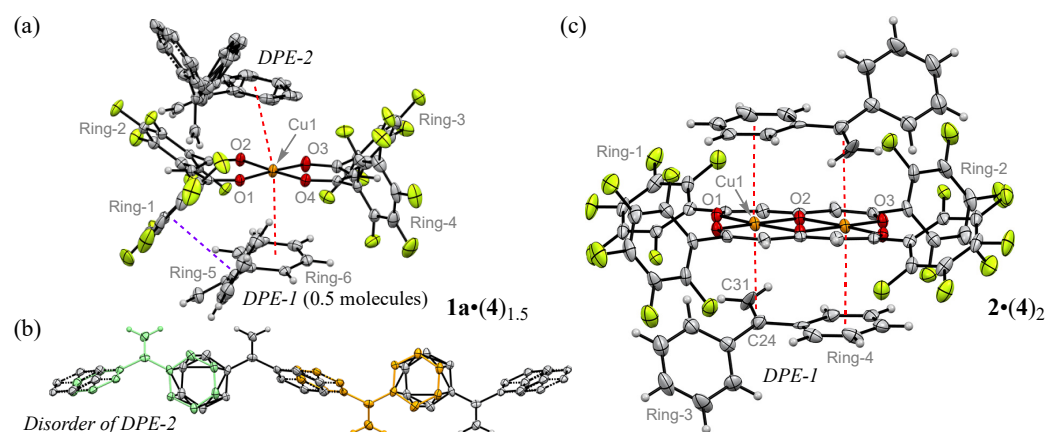


Figure 8. Crystal structures of (a) $1\mathbf{a}\bullet(4)_{1.5}$, (b) disordered structure of *DPE-2* in $1\mathbf{a}\bullet(4)_{1.5}$, and (c) $2\bullet(4)_2$, showing the atom-labeling schemes. Displacement ellipsoids are drawn at the 50% probability levels. The orange and purple dotted lines indicate $M\cdots\pi$ and π -hole $\cdots\pi$ interactions, respectively.

4. Conclusions

We have investigated the co-crystallization of the fully fluorinated coordination complex 1 and benzophenone 3 , resulting in two chiral crystals, $(1\mathbf{a})_2\bullet(3)_3$ and $(1\mathbf{b})_2\bullet(3)_3$, being obtained quantitatively. Remarkable π -hole $\cdots\pi$ and $M\cdots\pi$ interactions between the complex and the adaptable orientation of benzophenone were observed in both crystals, but thermal stabilities were different: the guest retention capability of $(1\mathbf{a})_2\bullet(3)_3$ is higher than that of $(1\mathbf{b})_2\bullet(3)_3$, which is dependent on the positive ESP values of the central metal ions. The corresponding crystal of $(1\mathbf{c})_2\bullet(3)_3$ is rarely obtained, and crystal separation was common, indicating weak intermolecular recognition due to the repulsion between the negative charges in the electron-rich regions of the Pt in $1\mathbf{c}$ and the phenyl ring in 3 . This phenomenon illustrates the effective encapsulation of large diphenyl compounds 3 in the crystal of the perfluorinated complexes, resulting in chiral crystals, $(1)_2\bullet(3)_3$. In this work, we also demonstrated the control of ESP through full fluorination to reverse the ESP from negative to positive for the Pd, which enriches our understanding of host–guest interactions using metal characteristics. Recognition of 3 within the crystal of metal complexes is generally assumed to involve coordination bonds between oxygen atoms' electron-rich sites and metal ions. However, this study demonstrates that electrostatic interactions, such as $M\cdots\pi$ interactions, play a crucial role in molecular recognition, as evidenced by comparative experiments with the dinuclear metal complex 2 and 1,1-diphenylethylene 4 , within the stronger electrophilic environment induced by fluorination. In molecular crystals acting as hosts, there is a competitive interplay between the affinity among host molecules and the affinity between host and guest molecules, allowing only those guest molecules that are electrostatically and structurally compatible to be incorporated within the crystal. In this study, we explored the formation of co-crystals and the interactions that could drive the process, using π -holes designed by the introduction of fluorine as molecular recognition sites. Enhancements in the electrophilicity of metal ions and a strengthening of $M\cdots\pi$

interactions were discovered. These advances in molecular recognition are anticipated to be valuable for the separation and purification of organic substances in future applications.

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Data Availability Statement: Crystallographic data have been deposited at CCDC; additional data are available in Appendix A.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and the deposition CCDC numbers are 1901579–1901580 and 2361541–2361545 for each crystal. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/structures/> (accessed on 24 June 2024).

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