

ELECTRONIC SUPPLEMENTARY INFORMATION

**Guest Encapsulations in Non-porous Crystals of Fully Fluorinated Dinuclear Metal Complexes with M<sub>2</sub>O<sub>2</sub> Core (M = Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>)**

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**S1. Preparations of 2, 3 and 4.**

(1) General.

All the chemicals were of reagent grade and used without further purification. Perfluorinated ligand HL and the corresponding dinuclear complexes, **3** and **4**, were prepared by previously described protocols of references 23 and 22, respectively. The results of the elemental analysis (EA) of C and H were determined by a Perkin-Elmer PE2400 analyzer.

(2) Preparation of **2**.

Dinuclear iron complex **2** was synthesized by combining of ligand HL, NaOMe, and FeCl<sub>2</sub>·4H<sub>2</sub>O in MeOH at room temperature for 1 h. After the reaction, the color of the solution changed from purple to red in the process of extraction using dichloromethane. The color change shows the oxidation of the central iron ions. After the solution was evaporated, the resulting red powder was crystallized using CH<sub>2</sub>Cl<sub>2</sub> to give red prismatic crystals. From the single crystal structure analysis, the crystal is monoclinic, *P*2<sub>1</sub>/*n* and the two metals crosslinked with methoxide ion having the composition of [Fe<sub>2</sub>L<sub>4</sub>(OMe)<sub>2</sub>]. Since cyclic voltammetry shows an irreversible reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, methoxide groups performed as anion sources in the complex.

(3) Preparations of **3** and **4** [ref.22]

Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and ligand HL were combined in an ethanol/CH<sub>2</sub>Cl<sub>2</sub> solution to give a red solution of dinuclear complexes [Co<sub>2</sub>L<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>] **3**. Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O and ligand HL were combined in the same condition to give green solution of dinuclear complexes [Ni<sub>2</sub>L<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>] **4**. The results of elemental analyses showed the formation of **3** (calcd. for C<sub>60</sub>H<sub>8</sub>Co<sub>2</sub>F<sub>40</sub>O<sub>10</sub> (%): C 40.79, H 0.46; found: C 40.85, H 0.56) and **4** (C<sub>60</sub>H<sub>8</sub>F<sub>40</sub>Ni<sub>2</sub>O<sub>10</sub> (%): C 40.81, H 0.46; found: C 40.98, H 0.47). These complexes were crystallized from CH<sub>2</sub>Cl<sub>2</sub> with the gas-phase diffusion of benzene to give red block crystals of **3**·2C<sub>6</sub>H<sub>6</sub> and green block crystals of **4**·2C<sub>6</sub>H<sub>6</sub>.

For all of the perfluorinated complexes **1-4**, the crystallizations of the complex without benzene derivatives were difficult to give powder and/or microcrystals, but the corresponding large single crystals were obtained with benzene (**a**) and CH<sub>2</sub>Cl<sub>2</sub> to give **1**·**3a**, **2**·**1.5a**, **3**·**2 a** and **4**·**2 a**, showing the high affinity of aromatic guest molecules.

**S2. Crystal data and structures of Fe<sup>3+</sup> complexes 2, 2•1.5a, 2•3b, 2•c, and 2•5d.**

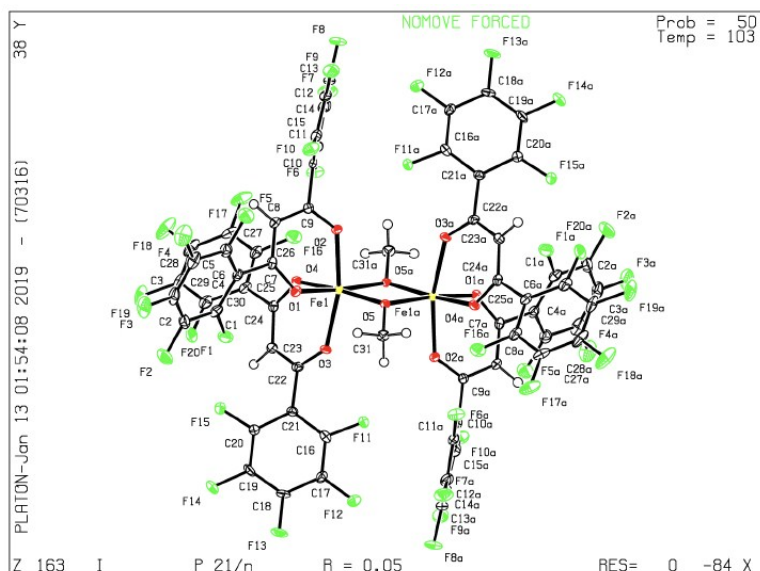
Guest encapsulations of benzene (**a**), toluene (**b**), p-xylene (**c**), and anisole (**d**) were examined by crystallization processes. Five single crystals of **2**, **2•1.5a**, **2•3b**, **2•c**, and **2•5d** were obtained from the crystallization of **2** in EtOH, benzene/CH<sub>2</sub>Cl<sub>2</sub>, toluene/CH<sub>2</sub>Cl<sub>2</sub>, p-xylene/CH<sub>2</sub>Cl<sub>2</sub>, and anisole/CH<sub>2</sub>Cl<sub>2</sub>, respectively. The crystal data were shown in Tables S1 and S2.

**Table S1.** Crystal data of **2** and **2•1.5a**.

	<b>2</b>	<b>2•1.5a</b>
Chemical formula	C <sub>62</sub> H <sub>10</sub> F <sub>40</sub> Fe <sub>2</sub> O <sub>10</sub>	C <sub>71</sub> H <sub>19</sub> F <sub>40</sub> Fe <sub>2</sub> O <sub>10</sub>
Description, color	block, red	prismatic, red
Crystal size	0.175x0.125x0.090	0.460x0.025x0.025
Formula weight	1786.40	1903.56
<i>T</i> [K]	103	103
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1
<i>a</i> [Å]	14.3286(12)	10.6384(13)
<i>b</i> [Å]	10.8784(10)	13.8709(16)
<i>c</i> [Å]	19.0990(14)	25.207(3)
$\alpha$ [°]	90	102.030(4)
$\beta$ [°]	98.836(3)	95.532(4)
$\gamma$ [°]	90	108.557(4)
<i>V</i> [Å <sup>3</sup> ]	2941.7(4)	3395.3(7)
<i>Z</i>	2	2
<i>D</i> <sub>c</sub> [g cm <sup>-3</sup> ]	2.017	1.862
<i>F</i> (000)	1748	1874
<i>R</i> <sub>int</sub>	0.0853	0.1215
Reflections measured	33678	44503
Reflections independent	4669	11990
GOF	1.100	1.007
<i>R</i> [( <i>I</i> ) > 2σ( <i>I</i> )]	0.0451	0.0623
<i>wR</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.0880	0.1592
CCDC No.	1906902	1894618

a) Molecular structure of **2**:

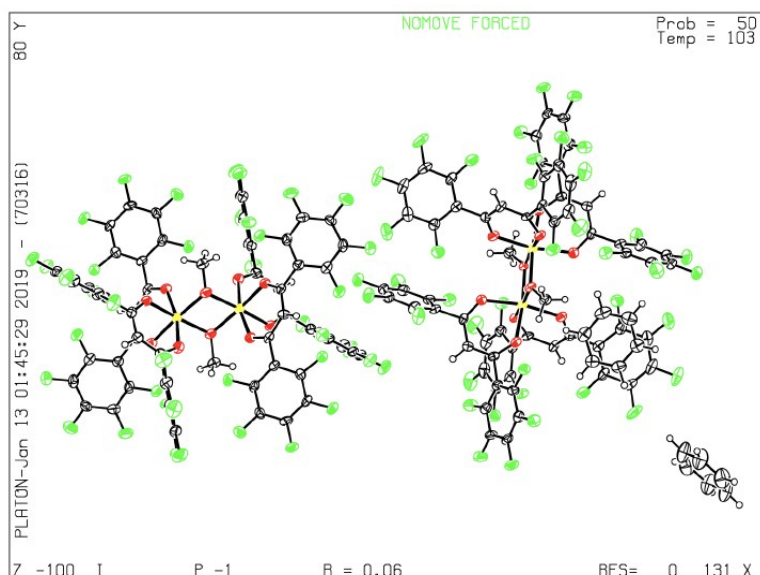
In the crystal (Figure S1), one half of the complex was observed as asymmetric unit. The whole complex was comprised as two iron(III) ions, four fluorinated ligands ( $C_{15}HF_{10}O_2^-$ ), and two methoxy ions ( $CH_3O^-$ ). H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms.



**Figure S1.** The molecular structure of **2** drawing by PLATON in checkCIF.

b) Molecular structure of **2**•1.5a:

In the crystal (Figure S2), two kinds of half complexes, a whole benzene, and a half of benzene were observed in asymmetric unit. The whole complex was comprised as two iron(III) ions, four fluorinated ligands ( $C_{15}HF_{10}O_2^-$ ), and two methoxy ions ( $CH_3O^-$ ). H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms.



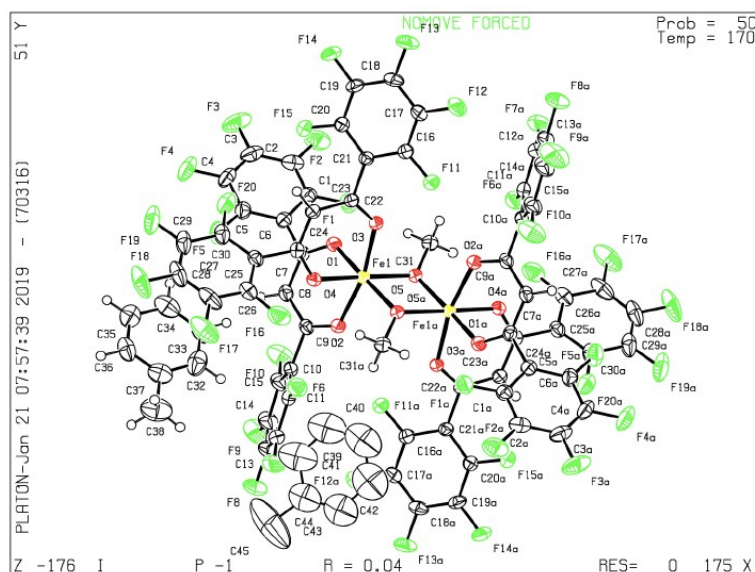
**Figure S2.** The molecular structure of **2**•1.5a drawing by PLATON in checkCIF.

**Table S2.** Crystal data of **2•3b**, **2•c**, and **2•5d**

	<b>2•3b</b>	<b>2•c</b>	<b>2•5d</b>
Chemical formula	C <sub>83</sub> H <sub>26</sub> F <sub>40</sub> Fe <sub>2</sub> O <sub>10</sub>	C <sub>70</sub> H <sub>20</sub> F <sub>40</sub> Fe <sub>2</sub> O <sub>10</sub>	C <sub>97</sub> H <sub>42</sub> F <sub>40</sub> Fe <sub>2</sub> O <sub>15</sub>
Description, color	block, red	plate, red	plate, red
Crystal size	0.351x0.256x0.240	0.164x0.154x0.094	0.194x0.187x0.126
Formula weight	2054.74	1892.56	2319.00
<i>T</i> [K]	170	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	10.8372(5)	10.4539(18)	13.1423(8)
<i>b</i> [Å]	12.9126(7)	12.401(2)	13.7532(6)
<i>c</i> [Å]	15.3274(8)	14.275(3)	14.2588(6)
$\alpha$ [°]	85.825(2)	93.903(5)	66.0600(10)
$\beta$ [°]	71.703(2)	108.901(5)	80.465(2)
$\gamma$ [°]	80.802(2)	95.072(5)	81.042(2)
<i>V</i> [Å <sup>3</sup> ]	2009.65(18)	1734.8(5)	2311.8(2)
<i>Z</i>	1	1	1
<i>D</i> <sub>c</sub> [g cm <sup>-3</sup> ]	1.698	1.812	1.666
<i>F</i> (000)	1016	932	1156
<i>R</i> <sub>int</sub>	0.0364	0.0454	0.1067
Reflections measured	23209	15360	26456
Reflections independent	7083	6003	8129
GOF	1.021	1.047	1.027
<i>R</i> [( <i>I</i> ) > 2σ( <i>I</i> )]	0.0358	0.0456	0.0666
<i>wR</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.0971	0.0996	0.1734
CCDC No.	1906903	1906904	1906905

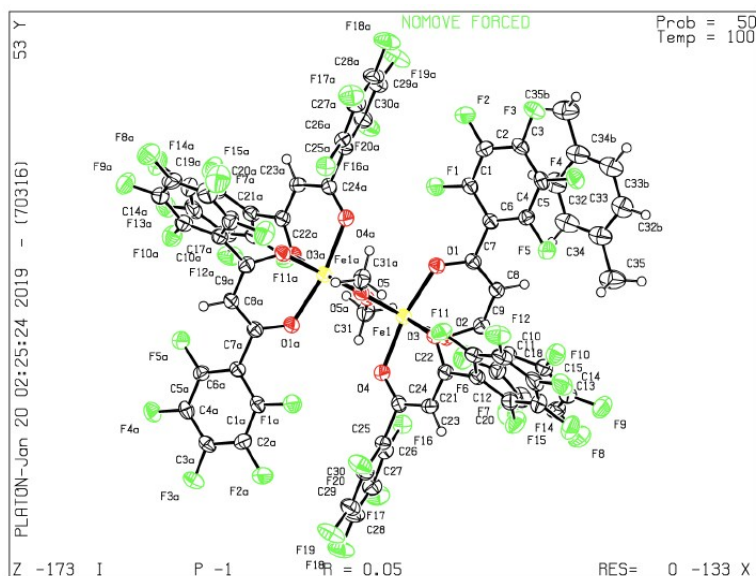
c) Molecular structure of **2•3b**:

In the crystal (Figure S3), three toluene molecules were observed as crystalline solvents; two whole toluenes (C32-C33-C34-C35-C36-C37-C38, toluene-1) and one half of toluene (C39-C40-C41-C42-C43-C44-C45, toluene-2). Since the toluene-2 sits on the inversion center, it is analyzed as 0.5 molecule as crystallographic disorder without the related protons. Thus, the moiety formula is C<sub>62</sub>H<sub>10</sub>F<sub>40</sub>Fe<sub>2</sub>O<sub>10</sub>•2(C<sub>7</sub>H<sub>8</sub>)•C<sub>7</sub>. H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms.

**Figure S3.** The molecular structure of **2•3b** drawing by PLATON in checkCIF.

d) Molecular structure of **2•c**:

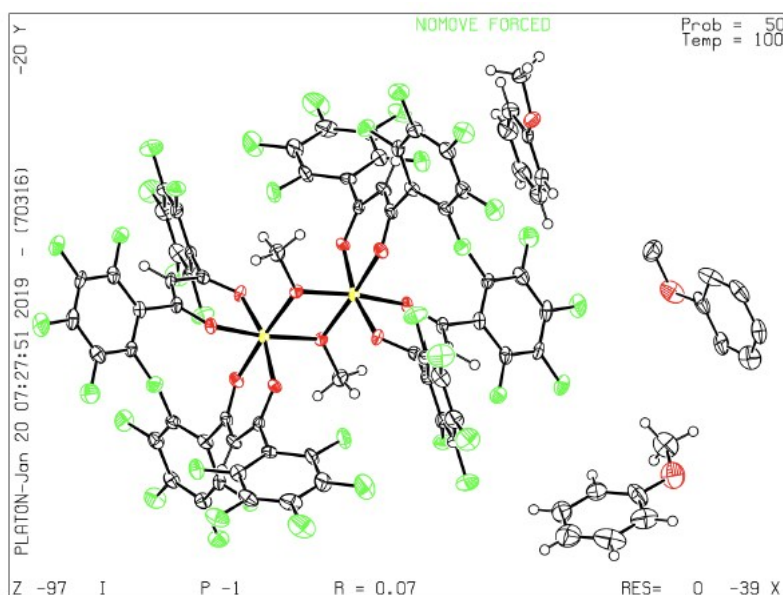
In the crystal (Figure S4), one half of the complex and one half of p-xylene were observed in asymmetric unit. H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms.



**Figure S4.** The molecular structure of **2•c** drawing by PLATON in checkCIF.

e) Molecular structure of **2•5d**:

In the crystal (Figure S5), three anisole molecules were observed as crystalline solvents; two whole anisoles (C32-C33-C34-C35-C36-C37-O6-C38, anisole-1) and one half of anisole (C39-C40-C41-C42-C43-C44-O7-C45, anisole-2). Since the anisole-2 sits on the inversion center, it is analyzed as 0.5 molecule as crystallographic disorder without the related protons. Thus, the moiety formula is  $C_{62}H_{10}F_{40}Fe_2O_{10} \cdot 2(C_7H_8O) \cdot C_7O$ . H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms.



**Figure S5.** The molecular structure of **2•5d** drawing by PLATON in checkCIF.

### S3. Crystal data and structures of Co<sup>2+</sup> and Ni<sup>2+</sup> complexes **3•3c**, **3•3d**, **4•3c** and **4•3d**.

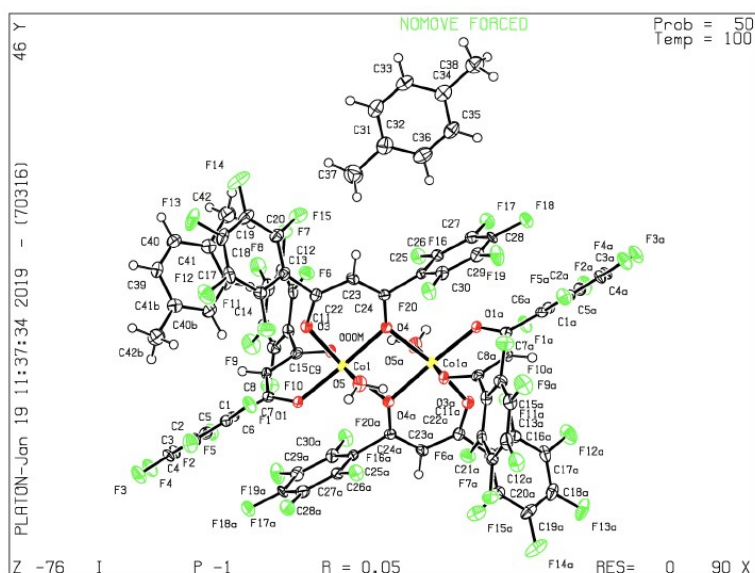
Single crystals of **3•3c**, **3•3d**, **4•3c**, and **4•3d** were obtained from the crystallization of **3** and **4** in EtOH, benzene/CH<sub>2</sub>Cl<sub>2</sub>, toluene/CH<sub>2</sub>Cl<sub>2</sub>, p-xylene/CH<sub>2</sub>Cl<sub>2</sub>, and anisole/CH<sub>2</sub>Cl<sub>2</sub>, respectively. The crystal data were shown in Tables S3.

**Table S3.** Crystal data of **3•3c**, **3•3d**, **4•3c**, and **4•3d**.

	<b>3•3c</b>	<b>3•3d</b>	<b>4•3c</b>	<b>4•3d</b>
Chemical formula	C <sub>84</sub> H <sub>38</sub> Co <sub>2</sub> F <sub>40</sub> O <sub>10</sub>	C <sub>81</sub> H <sub>24</sub> Co <sub>2</sub> F <sub>40</sub> O <sub>13</sub>	C <sub>84</sub> H <sub>38</sub> F <sub>40</sub> Ni <sub>2</sub> O <sub>10</sub>	C <sub>81</sub> H <sub>24</sub> F <sub>40</sub> Ni <sub>2</sub> O <sub>13</sub>
Description, color	block, red	prismatic, red	block, green	block, green
Crystal size	0.214x0.086x0.083	0.577x0.331x0.255	0.310x0.170x0.140	0.283x0.208x0.203
Formula weight	2085.00	2082.86	2084.56	2082.42
<i>T</i> [K]	100	100	150	100
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	11.2681(12)	11.3401(3)	11.3283(4)	11.3320(3)
<i>b</i> [Å]	12.2347(13)	12.6507(4)	12.2953(4)	12.6485(3)
<i>c</i> [Å]	15.0626(17)	14.9457(4)	14.9836(4)	14.8671(4)
$\alpha$ [°]	82.054(4)	84.837(1)	82.241(1)	84.882(1)
$\beta$ [°]	81.095(4)	80.425(1)	80.898(1)	80.385(1)
$\gamma$ [°]	75.236(3)	65.793(1)	75.304(1)	65.671(1)
<i>V</i> [Å <sup>3</sup> ]	1973.2(4)	1927.77(10)	1983.42(11)	1913.94(9)
<i>Z</i>	1	1	1	1
<i>D</i> <sub>c</sub> [g cm <sup>-3</sup> ]	1.755	1.794	1.745	1.807
<i>F</i> (000)	1036	1028	1038	1030
<i>R</i> <sub>int</sub>	0.0864	0.0215	0.0405	0.0276
Reflections measured	22049	21915	22974	22126
Reflections independent	6955	6793	6992	6753
GOF	1.043	1.062	1.065	1.060
<i>R</i> [( <i>I</i> ) > 2σ( <i>I</i> )]	0.0529	0.0298	0.0354	0.0306
<i>wR</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.1162	0.0799	0.0778	0.0746
CCDC No.	1906906	1906907	1906908	1906909

#### f) Molecular structure of **3•3c**:

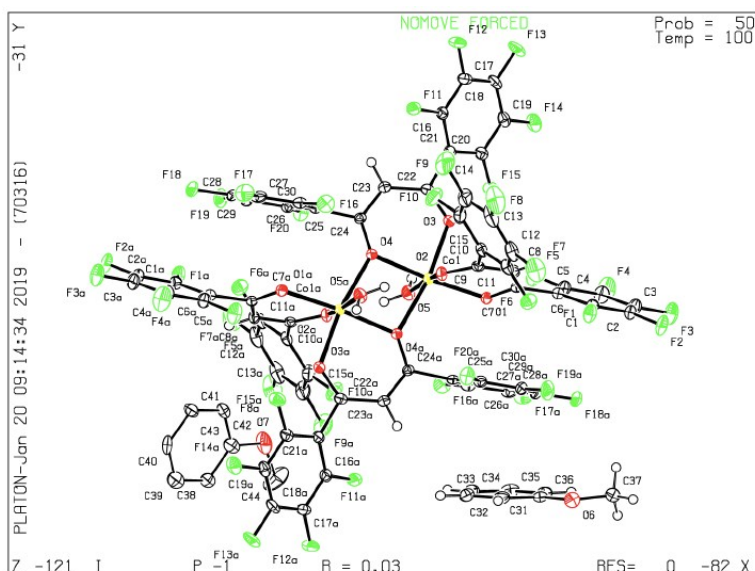
In the crystal (Figure S6), one half of the complex, a whole p-xylene, and one half of p-xylene were observed in asymmetric unit. The whole complex was comprised as two cobalt(II) ions, four fluorinated ligands (C<sub>15</sub>HF<sub>10</sub>O<sub>2</sub><sup>-</sup>), and two water molecules (H<sub>2</sub>O). H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms. Water atoms H5A and H5B were located in a difference Fourier density map and were refined freely [O5-H5A = 0.85(7) Å and O5-H5B = 0.87(6) Å].



**Figure S6.** The molecular structure of **3•3c** drawing by PLATON in checkCIF.

g) Molecular structure of **3•3d**:

In the crystal (Figure S7), three anisole molecules were observed as crystalline solvents; two whole anisoles (C31-C32-C33-C34-C35-C36-O6-C37, anisole-1) and one half of anisole (C38-C39-C40-C41-C42-C43-O7-C44, anisole-2). Since the anisole-2 sits on the inversion center, it is analyzed as 0.5 molecule as crystallographic disorder without the related protons. Thus, the moiety formula is  $C_{60}H_8Co_2F_{40}O_{10} \cdot 2(C_7H_8O) \cdot C_7O$ . H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms. Water atoms H5A and H5B were located in a difference Fourier density map and were refined freely [O5-H5A = 0.83(3) Å and O5-H5B = 0.84(3) Å].

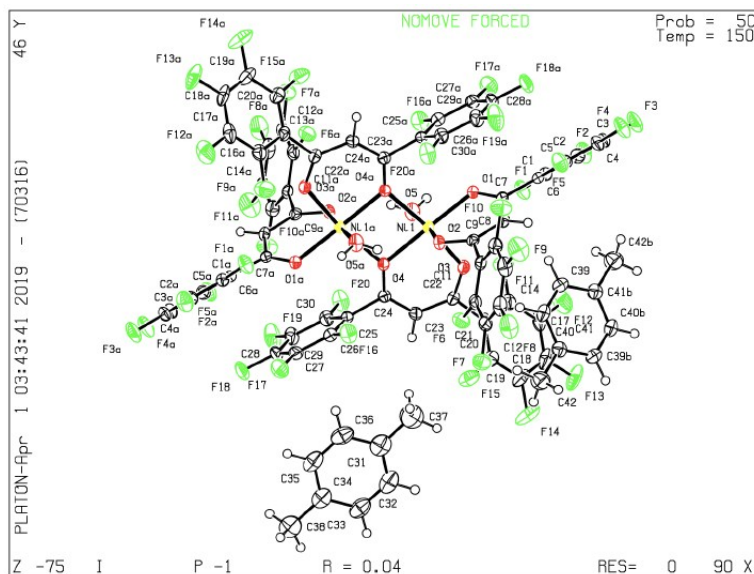


**Figure S7.** The molecular structure of **3•3d** drawing by PLATON in checkCIF.



h) Molecular structure of **4•3c**:

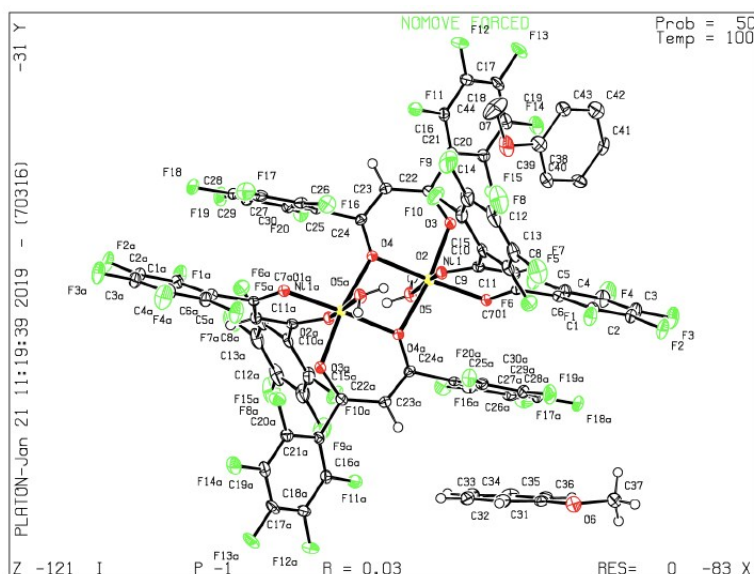
In the crystal (Figure S8), one half of the complex, a whole p-xylene, and one half of p-xylene were observed in asymmetric unit. The whole complex was comprised as two nickel(II) ions, four fluorinated ligands ( $C_{15}HF_{10}O_2^-$ ), and two water molecules ( $H_2O$ ). H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms. Water atoms H5A and H5B were located in a difference Fourier density map and were refined freely [O5-H5A = 0.91(4) Å and O5-H5B = 0.78(3) Å].



**Figure S8.** The molecular structure of **4•3c** drawing by PLATON in checkCIF.

i) Molecular and packing structures of **4•3d**:

In the crystal (Figure S9), three anisole molecules were observed as crystalline solvents; two whole anisoles (C31-C32-C33-C34-C35-C36-O6-C37, anisole-1) and one half of anisole (C38-C39-C40-C41-C42-C43-O7-C44, anisole-2). Since the anisole-2 sits on the inversion center, it is analyzed as 0.5 molecule as crystallographic disorder without the related protons. Thus, the moiety formula is  $C_{60}H_8Co_2F_{40}O_{10} \cdot 2(C_7H_8O) \cdot C_7O$ . H atoms attached to C atoms were refined as riding on their idealized positions, with C-H = 0.95 Å and 0.98 Å for aromatic and aliphatic atoms. Water atoms H5A and H5B were located in a difference Fourier density map and were refined freely [O5-H5A = 0.91(3) Å and O5-H5B = 0.79(3) Å]. This crystal is isomorph of the corresponding cobalt complex of **3•(8)**<sub>3</sub>.



**Figure S9.** The molecular structure of **4•3d** drawing by PLATON in checkCIF.



#### S4. Summary of the mainly contributed intermolecular interactions in the crystals.

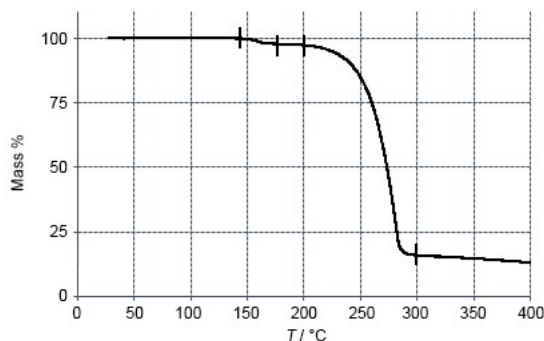
The remarkable intermolecular interactions were extracted from the PLATON data analysis.

crystals	arene-perfluoroarene	C-F $\cdots\pi$ (C <sub>6</sub> F <sub>5</sub> )	C-F $\cdots$ H-C (F $\cdots$ C)	another interaction
<b>2</b>	no	exist (3.18, 3.25 Å)	no	weak $\pi$ (C <sub>6</sub> F <sub>5</sub> ) $\cdots\pi$ (C <sub>6</sub> F <sub>5</sub> )
<b>2•1.5a</b>	exist (3.61 Å)	exist (3.21, 3.28 Å)	no	$\pi$ (C <sub>6</sub> F <sub>5</sub> ) $\cdots\pi$ (C <sub>6</sub> F <sub>5</sub> )
<b>2•3b</b>	exist (3.59, 3.63 Å)	exist (3.02, 3.38 Å)	no	$\pi$ (C <sub>6</sub> F <sub>5</sub> ) $\cdots\pi$ (C <sub>6</sub> F <sub>5</sub> )
<b>2•c</b>	possible (3.74 Å)	exist (3.40, 3.57 Å)	no	$\pi$ (C <sub>6</sub> F <sub>5</sub> ) $\cdots\pi$ (C <sub>6</sub> F <sub>5</sub> )
<b>2•5d</b>	exist (3.56, 3.62 Å)	exist (3.24, 3.46 Å)	exist (3.01 Å)	---
<b>3•3c</b>	exist (3.44 Å)	exist (3.25, 3.37 Å)	exist (3.24 Å)	CH $\cdots\pi$ (C <sub>6</sub> H <sub>4</sub> )
<b>3•3d</b>	exist (3.47, 3.57 Å)	exist (3.29, 3.34 Å)	exist (3.05, 3.16 Å)	CH $\cdots\pi$ (C <sub>6</sub> H <sub>5</sub> )
<b>4•3c</b>	exist (3.44 Å)	exist (3.22 Å)	exist (3.22, 3.38 Å)	CH $\cdots\pi$ (C <sub>6</sub> H <sub>4</sub> )
<b>4•3d</b>	exist (3.46, 3.57 Å)	exist (3.26, 3.35 Å)	exist (3.03, 3.16 Å)	CH $\cdots\pi$ (C <sub>6</sub> H <sub>5</sub> )

#### S5. TG data for 2, 3, and 4 without guest molecules at the scanning rates 5 °C min<sup>-1</sup>.

All the TG results in this article are shown at the same scanning rate, 5 °C min<sup>-1</sup>, for the comparison.

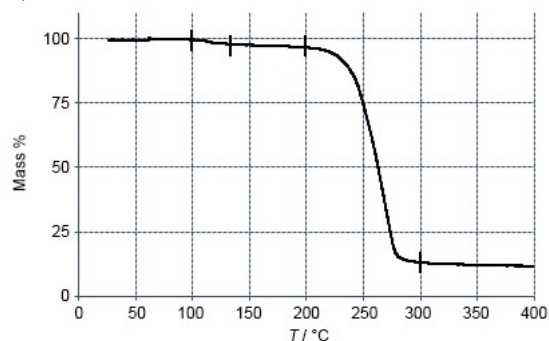
##### a) TG of 2



140 °C (99.8 wt%), 175 °C (97.7 wt%),  
200 °C (97.2 wt%), 300 °C (16.0 wt%)

Found: -2.3 wt% (~175 °C), and quickly decomposed.  
Calcd.: -3.5 wt% for two CH<sub>3</sub>O groups.

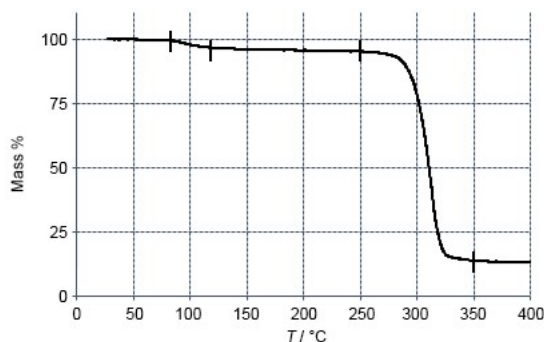
##### b) TG of 3



100 °C (99.4 wt%), 130 °C (97.8 wt%),  
200 °C (96.4 wt%), 300 °C (13.2 wt%)

Found: -2.2 wt% (~130 °C), and quickly decomposed.  
Calcd.: -2.0 wt% for two H<sub>2</sub>O molecules.

##### c) TG of 4



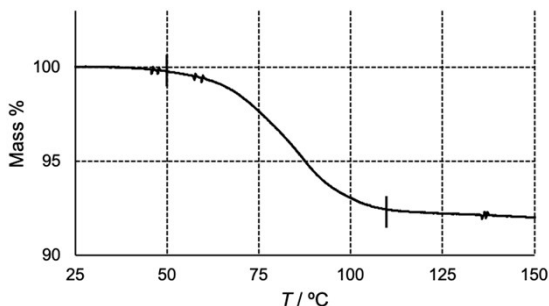
80 °C (99.5 wt%), 120 °C (96.6 wt%), 250 °C (95.2 wt%), 350 °C (14.0 wt%)

Found: -3.4 wt% (~120 °C), and slowly decomposed at 250 °C.  
Calcd.: -2.0 wt% for two H<sub>2</sub>O molecules.

### S6. TG curves of the guest releases at the scanning rates 5 °C min<sup>-1</sup>.

All the TG results in this article are shown at the same scanning rate, 5 °C min<sup>-1</sup>, for the comparison.

a) TG of **2•1.5a**

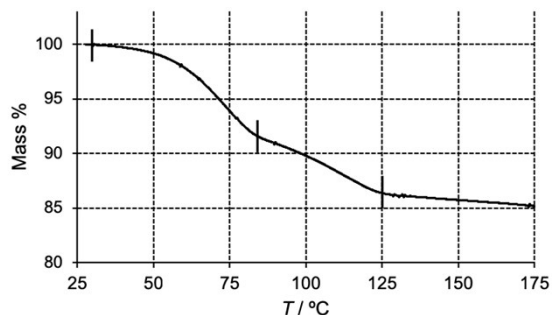


50 °C (99.7 wt%), 110 °C (92.4 wt%)

Found: -7.3 wt% (50 °C-110 °C)

Calcd.: -6.2 wt% for 1.5 benzene molecules

b) TG of **2•3b**

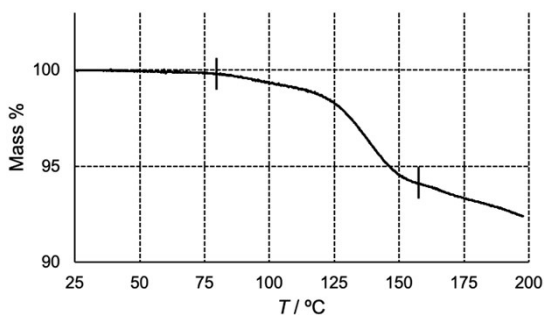


30 °C (99.9 wt%), 80 °C (92.4 wt%), 125 °C (86.3 wt%)

Found: -13.6 wt% (30 °C-125 °C)

Calcd.: -13.4 wt% for 3 toluene molecules

c) TG of **2•c**

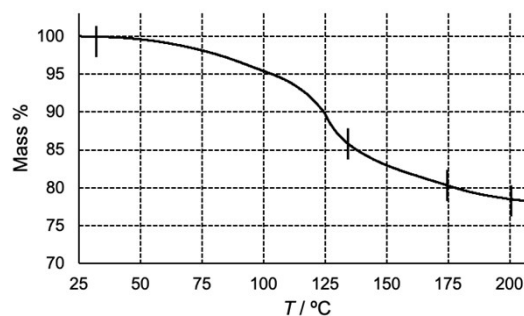


80 °C (99.7 wt%), 160 °C (94.0 wt%)

Found: -5.7 wt% (80 °C-110 °C)

Calcd.: -5.6 wt% for 1 p-xylene molecule

d) TG of **2•5d**

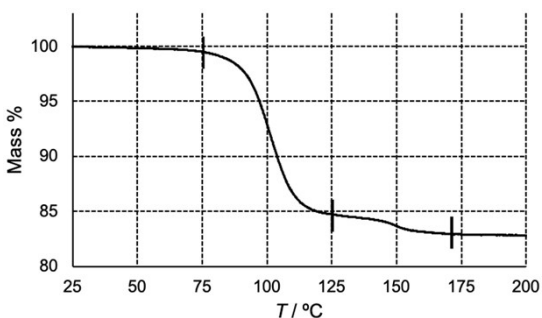


30 °C (99.9 wt%), 130 °C (87.1 wt%),  
175 °C (80.2 wt%), 200 °C (78.5 wt%)

Found: -21.4 wt% (30 °C-200 °C)

Calcd.: -23.2 wt% for 5 anisole molecules

e) TG of **3•3c**

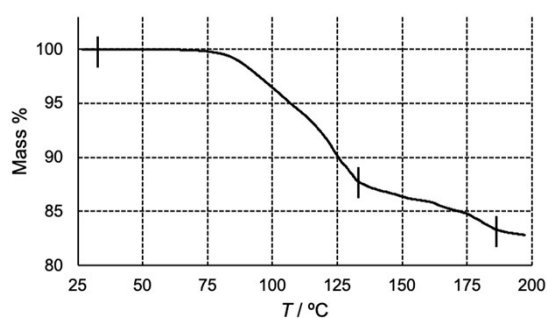


75 °C (99.4wt%),125 °C (84.7 wt%),  
170 °C (82.9 wt%)

Found: -14.7 wt% (75 °C-125 °C)

Calcd.: -15.3 wt% for 3 p-xylene molecules

f) TG of **3•3d**

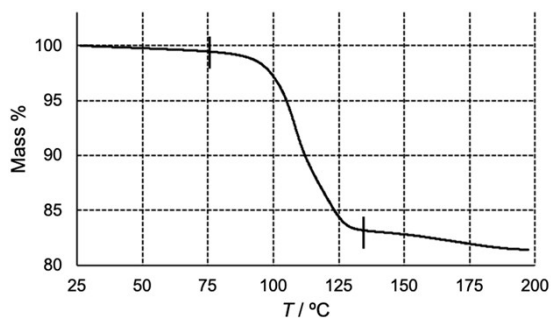


30 °C (99.9 wt%), 130 °C (88.5 wt%),  
180 °C (84.1 wt%)

Found: -15.8 wt% (30 °C-180 °C)

Calcd.: -15.5wt% for 3 anisole molecules

g) TG of **4•3c**

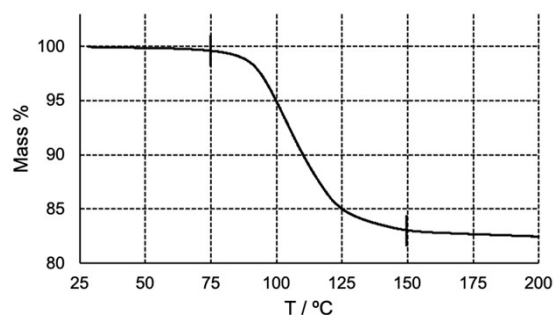


75 °C (99.4 wt%), 130 °C (83.4 wt%)

Found: -16.0 wt% (75 °C-130 °C)

Calcd.: -15.3 wt% for 3 p-xylene molecules

h) TG of **4•3d**



75 °C (99.5 wt%), 150 °C (83.0 wt%)

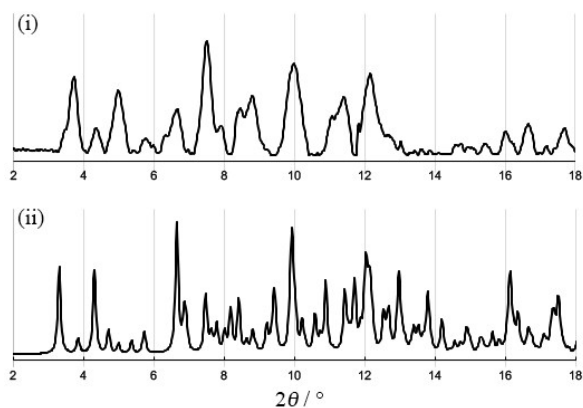
Found: -16.5 wt% (75 °C-150 °C)

Calcd.: -15.5 wt% for 3 anisole molecules

**S7. XRD of powder samples 2 and 2•1.5a.**

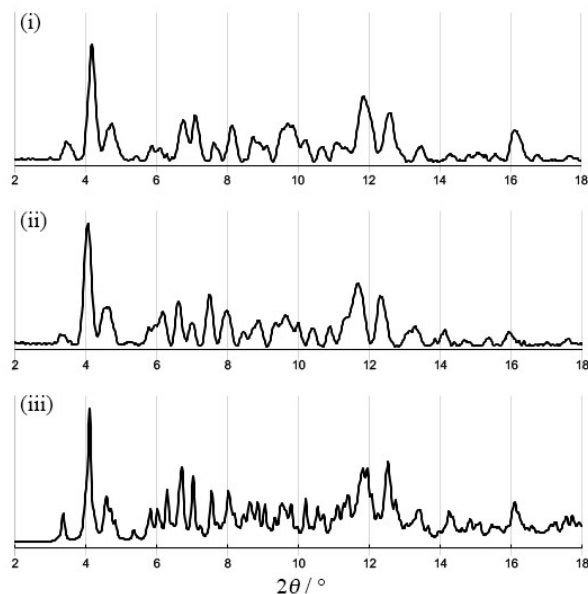
All the crystals and powders were measured by powder XRD with D8 QUEST (MoK $\alpha$ ,  $\lambda = 0.7013 \text{ \AA}$ ).

a) XRD and simulation patterns of **2**



(i) pXRD of powder sample **2** and (ii) simulation of single-crystal structure of **2** at 100 K.

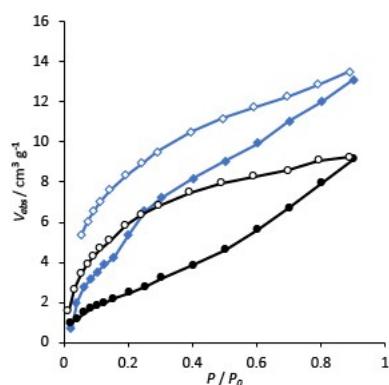
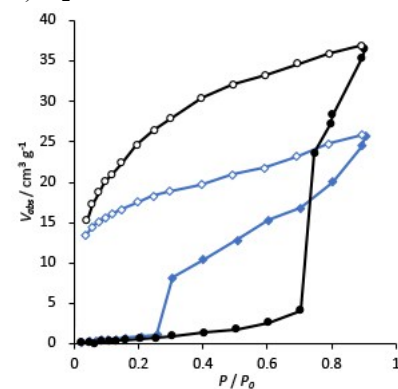
b) XRD and simulation patterns of **2•1.5a**



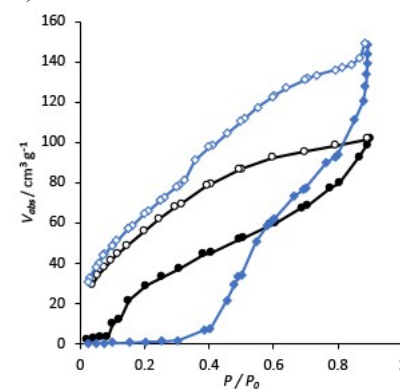
(i) pXRD of powder sample **2•1.5a**, (ii) benzene reinsertion for **2**, and (iii) simulation of single-crystal structure of **2•1.5a** at 100 K. The results of (i) and (ii) shows the reversible benzene encapsulations for **2**.

**S8. Gas adsorption isotherms of 3 and 4.**

Gas adsorption isotherm of Ni<sup>2+</sup> complex **4** is shown as blue colors (the corresponding Co<sup>2+</sup> complex **3** is black). The adsorption/desorption behavior of the complexes were examined on microcrystalline powder samples, which were activated by heating at 60 °C for 3 h under vacuum.

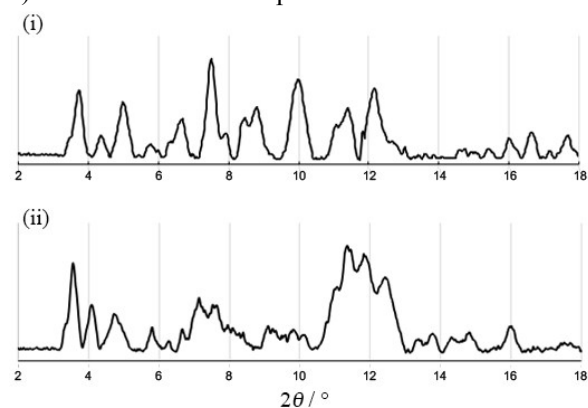
a) CO<sub>2</sub> at 195 Kb) O<sub>2</sub> at 90 K

c) NO at 121 K

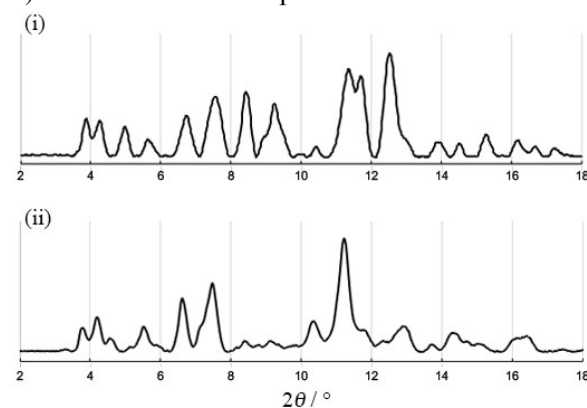


### S9. XRD of powder samples 2-4 after gas adsorptions.

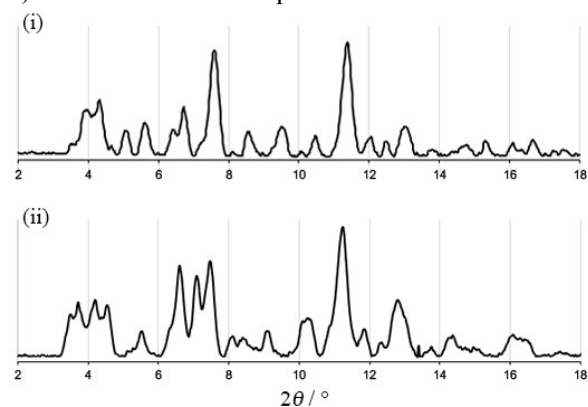
All powder diffractions were measured by D8 QUEST (MoK $\alpha$ ,  $\lambda = 0.7013 \text{ \AA}$ ) to compare with the solvated crystals. Unfortunately, the crystalline properties of the complexes **2-4** in the absence of guest is low and changed the patterns because of the flexible molecular crystals.

a) XRD and simulation patterns of **2**

(i) After and (ii) before gas adsorption of **2** at 160 and 100 K, respectively.

b) XRD and simulation patterns of **3**

(i) After and (ii) before gas adsorption of **3** at 160 and 100 K, respectively.

c) XRD and simulation patterns of **4**

(i) After and (ii) before gas adsorption of **4** at 160 and 100 K, respectively.