

## Structural controls of 2D sheet copper(I) ethylene and carbonyl coordination polymers directed by anions and solvents<sup>†</sup>

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The reactions of Cu(I) ion with  $\{\text{BF}_4^-\text{, ClO}_4^-\text{, or PF}_6^-\}$  anions and 6,6'-dimethyl-4,4'-bipyrimidine (Me<sub>2</sub>bpm) under C<sub>2</sub>H<sub>4</sub> or CO in MeOH preferentially afforded three 2D sheet Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts  $[\text{Cu}_4(\text{Me}_2\text{bpm})_3(\text{C}_2\text{H}_4)_3(\text{MeCN})](\text{BF}_4)^-\cdot 0.33\text{MeOH}]_n$  (**2**),  $\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3(\text{C}_2\text{H}_4)_3(\text{MeOH})_{0.33}](\text{ClO}_4)_4\}_n$  (**3**), and  $\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3(\text{CO})_3(\text{MeCN})](\text{PF}_6)_4\cdot 0.33\text{MeCN}\}_n$  (**4**), whereas the similar reaction of Cu(I) ion with a BF<sub>4</sub><sup>-</sup> anion and Me<sub>2</sub>bpm under CO in MeOH gave the metallamacrocyclic tetranuclear Cu(I)–Me<sub>2</sub>bpm/CO adduct  $[\text{Cu}_4(\text{Me}_2\text{bpm})_4(\text{CO})_4](\text{BF}_4)_4\cdot 4\text{MeOH}$  (**5**). In Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts **2–4**, it should be noted that the metallacalix[3]arene structures of the  $[\text{Cu}_3(\text{Me}_2\text{bpm})_3]^{3+}$  framework are linked through another Cu atom with MeCN (**2** and **4**) or MeOH (**3**) to produce a chiral 2D sheet structure with small Cu<sub>3</sub> and large Cu<sub>9</sub> cavities. In the small triangular Cu<sub>3</sub> cavities, one MeOH (**2**) or MeCN (**4**) molecule is encapsulated in complexes **2** and **4**, whereas these Cu<sub>3</sub> cavities are empty in complex **3**. In the large Cu<sub>9</sub> cavities, one anion (X = BF<sub>4</sub><sup>-</sup> (**2**), ClO<sub>4</sub><sup>-</sup> (**3**) or PF<sub>6</sub><sup>-</sup> (**4**)) is surrounded by six Me groups of three Me<sub>2</sub>bpm on the upside and three anions (X) are functionally accommodated on the downside for complexes **2–4**, respectively. In the Cu(I)–Me<sub>2</sub>bpm/CO adduct **5**, two of the four BF<sub>4</sub><sup>-</sup> anions are accommodated in the upper and lower cavities of the [Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>4</sub>] framework. We demonstrated that the metallamacrocyclic and polymeric 2D sheet Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts can be reasonably self-assembled under the direction of anions and solvents.

### Introduction

The use of chemical templates is now a powerful approach to the rational synthesis of inorganic and organic molecular assemblies.<sup>1</sup> This strategy not only enables the synthesis of molecules in a more efficient manner but also aids in the preparation of assemblies that have unusual topologies, such as macrocycles, molecular cages, interlocked species (such as catenanes and rotaxanes), and helical assemblies. In order for a template process to successfully yield the targeted product, the structural and electrostatic properties of the template need to be selected carefully. From a structural point of view, both the size and

geometry of the template have to be considered, while electrostatically the choice is restricted to neutral, positively charged or negatively charged species. Although cationic and neutral species have been widely used as templates in synthetic chemistry, the role of anion templates was scarcely exploited until the second half of the 1990s. This relative lack of an anion-templated process is partially attributable to the complicated physicochemical nature of the anions, such as their diffuse nature, variety of geometries, pH sensitivity, and relatively high solvation-free energies. However, the potential use of anion species as templates has been recently argued in a wide range of novel inorganic and organic assemblies.<sup>2</sup>

4,4'-Bipyrimidine (bpm) and its derivatives are an attractive nitrogen ligand with a bidentate site for chelation and two *exo* N-donor sites for bridging, since it can be thought of as a combination of 2,2'-bipyridine and 4,4'-bipyridine.<sup>3,4</sup> It is expected to produce both finite metallamacrocyclic and infinite polymeric compounds with square/rectangular motifs. We recently reported that the combination of Cu(I) ion and bpm can produce a diversity of polymeric Cu(I)–bpm/C<sub>2</sub>H<sub>4</sub> adducts and Cu(I)–bpm cage compounds by the choice of anions and solvent (Scheme 1(a)).<sup>4a</sup> In particular, the reaction of the Cu(I) ion with a BF<sub>4</sub><sup>-</sup> anion and bpm under C<sub>2</sub>H<sub>4</sub> in MeOH afforded the first chiral 2D sheet Cu(I)–C<sub>2</sub>H<sub>4</sub> coordination polymer

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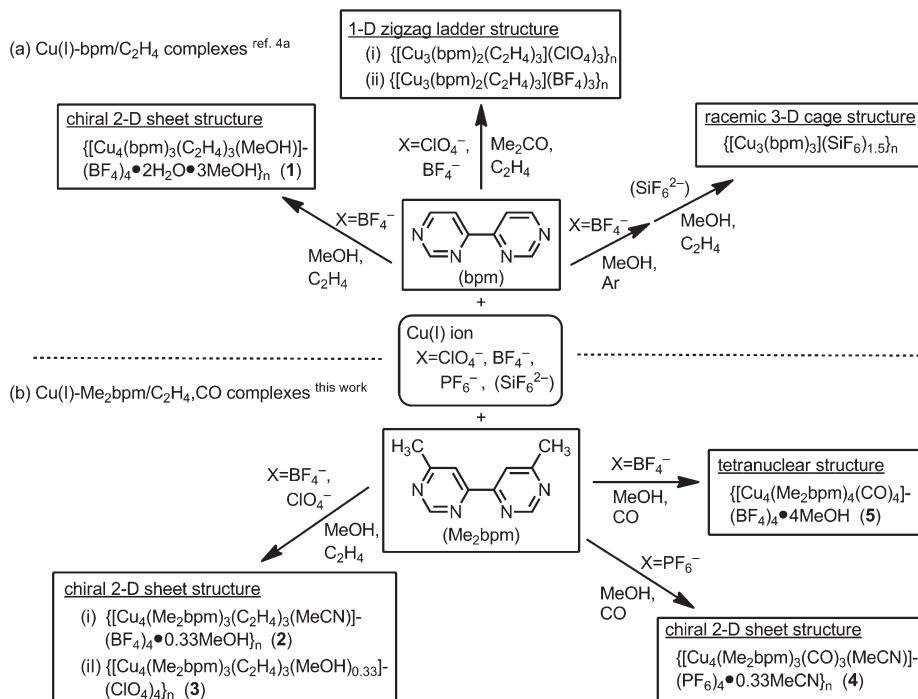
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<sup>†</sup> Electronic supplementary information (ESI) available: Crystal packing structures of complexes **3** and **4** were deposited in Fig. S1 and S2. CCDC 866528–866531 for complexes **2–5**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25211b.



**Scheme 1** Cu(I)-bpm/C<sub>2</sub>H<sub>4</sub> and Cu(I)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes.

{[Cu<sub>4</sub>(bpm)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(MeOH)](BF<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O·3MeOH}<sub>n</sub> (**1**). However, structurally Cu(I)-C<sub>2</sub>H<sub>4</sub> adducts have been poorly characterized because of the extremely labile nature of the Cu(I)-C<sub>2</sub>H<sub>4</sub> interaction.<sup>4,5</sup> In particular, there have been few preparative and structural reports on polynuclear and polymeric Cu(I)-C<sub>2</sub>H<sub>4</sub> complexes.<sup>4,5e,f</sup> In this study, we attempted to realize a reasonably preparative approach to self-assemble 2D sheet Cu(I)-C<sub>2</sub>H<sub>4</sub> adducts under the direction of anions and solvents by promoting the preliminary knowledge in Cu(I)-bpm/C<sub>2</sub>H<sub>4</sub> adducts.<sup>4a</sup> As a further investigation, four novel Cu(I)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts were prepared by the combination of a Cu(I) ion with {BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>} anions and 6,6'-dimethyl-4,4'-bipyrimidine (Me<sub>2</sub>bpm) as a related bpm ligand under C<sub>2</sub>H<sub>4</sub> or CO (Scheme 1(b)). Their crystal structures and properties were characterized by X-ray, IR, XRPD, and TG-DTA analyses.

## Experimental sections

### General procedures and reagents

[Cu(MeCN)<sub>4</sub>]X (X = PF<sub>6</sub> and BF<sub>4</sub>) were prepared according to the literature.<sup>6</sup> The 6,6'-dimethyl-4,4'-bipyrimidine (Me<sub>2</sub>bpm) ligand was prepared with modifications of the literature method.<sup>7</sup> Pure C<sub>2</sub>H<sub>4</sub> and CO gases (>99.9%) were purchased from Sumitomo Seika Chemicals (Japan). All organic solvents were dried and distilled by the usual methods before use. All procedures were carried out using standard Schlenk techniques under C<sub>2</sub>H<sub>4</sub> or CO. IR spectra were recorded with a JASCO FT-IR 430 spectrometer as KBr pellets. Thermogravimetric analysis (TG-DTA) was carried out with a RIGAKU Thermo Plus 8120 under flowing N<sub>2</sub> gas.

### Preparation of Cu(I)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes

{[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(MeCN)](BF<sub>4</sub>)<sub>4</sub>·0.33MeOH}<sub>n</sub> (**2**). [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (62.9 mg, 0.20 mmol) and Me<sub>2</sub>bpm

(3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under C<sub>2</sub>H<sub>4</sub>. The yellow reaction solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under C<sub>2</sub>H<sub>4</sub>. The reaction solution was allowed to stand for one week at -10 °C, after which red brick crystals of complex **2** were collected. After complex **2** was dried by flowing C<sub>2</sub>H<sub>4</sub> gas, it was subjected immediately to elementary analysis, IR, XRPD, and TG-DTA. Anal. Calcd. for Cu<sub>4</sub>C<sub>38.32</sub>H<sub>43.32</sub>N<sub>13</sub>O<sub>0.33</sub>B<sub>4</sub>F<sub>16</sub>: C, 35.53; H, 3.60; N, 14.05. Found: C, 35.30; H, 3.81; N, 13.83. IR (KBr, cm<sup>-1</sup>): 1597(s), 1542(s, C<sub>2</sub>H<sub>4</sub>), 1520(m), 1468(m), 1441(m), 1420(m), 1378(m), 1346(s, C<sub>2</sub>H<sub>4</sub>), 1307(m), 1259(s), 1230(m), 1030(s, BF<sub>4</sub>), 877(s), 748(m), 679(m), 553(m), 533(m), 522(m), 404(s).

{[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(MeOH)<sub>0.33</sub>](ClO<sub>4</sub>)<sub>4</sub>}<sub>n</sub> (**3**). The precursor Cu(I)-C<sub>2</sub>H<sub>4</sub> complex [Cu(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>]ClO<sub>4</sub> was prepared by the reductive reaction of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (37.1 mg, 0.10 mmol) with Cu wire in MeOH (5 ml) under C<sub>2</sub>H<sub>4</sub>. A 5 ml MeOH solution of Me<sub>2</sub>bpm (5.5 mg, 0.03 mmol) was added to the above Cu(I)-C<sub>2</sub>H<sub>4</sub> solution. The C<sub>2</sub>H<sub>4</sub> gas was then bubbled for 30 mins. The resultant yellow solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under C<sub>2</sub>H<sub>4</sub>. The reaction solution was allowed to stand at -10 °C for one week, after which red plate crystals of complex **3** were collected. After complex **3** was dried by flowing C<sub>2</sub>H<sub>4</sub> gas, it was subjected immediately to elementary analysis and IR. Anal. Calcd. for Cu<sub>4</sub>C<sub>36.33</sub>H<sub>42</sub>N<sub>12</sub>O<sub>16.33</sub>Cl<sub>4</sub>: C, 33.43; H, 3.34; N, 12.88. Found: C, 34.15; H, 3.85; N, 12.38. IR (KBr, cm<sup>-1</sup>): 1599(s), 1543(m, C<sub>2</sub>H<sub>4</sub>), 1525(m), 1468(w), 1425(m), 1392(w), 1360(w, C<sub>2</sub>H<sub>4</sub>), 1308(w), 1259(m), 1231(w), 1089–1030(s, ClO<sub>4</sub>), 877(m), 747(m), 691(w), 679(w), 636(m), 624(s), 553(w), 536(w), 404(m).

*Caution! Perchlorate salts of metal complexes with organic compounds are potentially explosive! Only small amounts of*

materials should be prepared, and they should be handled with great care.

**[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>3</sub>(CO)<sub>3</sub>(MeCN)](PF<sub>6</sub>)<sub>4</sub>·0.33MeCN** (4). [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (37.3 mg, 0.10 mmol) and Me<sub>2</sub>bpm (3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under CO. The colorless reaction solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under CO. The reaction solution was allowed to stand for 2 weeks at -30 °C, and dark reddish-brown crystals of complex 4 were obtained. After complex 4 was dried by flowing CO gas, it was subjected immediately to elementary analysis, IR, and TG-DTA. Anal. Calcd. for Cu<sub>4</sub>C<sub>37</sub>N<sub>14</sub>H<sub>36</sub>O<sub>3</sub>P<sub>4</sub> F<sub>24</sub>: C, 28.51; H, 2.32; N, 12.58. Found: C, 28.18; H, 2.53; N, 12.01. IR (KBr, cm<sup>-1</sup>): 2126(s, CO), 1618(s, 1550(s), 1526(s), 1479(s), 1428(s), 1402(s), 1361(m), 1311(m), 1277(m), 1193(m), 1101(m), 1053(m), 1034(s), 840(s, PF<sub>6</sub>), 746(s), 690(m), 556(s), 421(m).

**[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>4</sub>(CO)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub>·4MeOH** (5). [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (31.5 mg, 0.10 mmol) and Me<sub>2</sub>bpm (3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under CO. The pale yellow reaction solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under CO. The reaction solution was allowed to stand for 2 weeks at -30 °C, and yellowish-brown crystals of complex 5 were obtained. After complex 5 was dried by flowing CO gas, it was subjected immediately to elementary analysis, IR, and TG-DTA. Anal. Calcd. for Cu<sub>4</sub>C<sub>48</sub>H<sub>56</sub>N<sub>16</sub>O<sub>8</sub>B<sub>4</sub>F<sub>16</sub>: C, 36.34; H, 3.56; N, 14.13. Found: C, 36.25; H, 3.22; N, 14.15. IR (KBr, cm<sup>-1</sup>): 2111(s, CO), 1628(s), 1544(s), 1478(m), 1440(m), 1400(m), 1360(m), 1313(w), 1273(w), 1234(w), 1061(s, BF<sub>4</sub>), 889(m), 851(w), 748(w), 686(w), 566(w), 518(w), 415(w).

### X-ray crystal structure determinations

All measurements of Cu(I)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes 2-5 were made on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ( $\lambda = 0.71070 \text{ \AA}$ ). The diffraction data were collected at -143(2), -154(2), -153(2), and -153(2) °C for complexes 2-5 by the ω scan mode, respectively. Of the 14 763, 9878, 20 146, and 10 806 reflections collected, 3920, 3420, 4212, and 4141 were unique ( $R_{\text{int}} = 0.0232$ , 0.0385, 0.0401, and 0.0245) for complexes 2-5, respectively. Data were collected and processed using the Crystal Clear program (Rigaku). The linear absorption coefficients,  $\mu$ , for Mo-Kα radiation were 17.33, 19.26, 17.72, and 13.47 cm<sup>-1</sup> for complexes 2-5, respectively. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method (SHELXS-97) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included and were constrained to the ideal position and thermal displacement parameter. In complex 2, the crystal structure was refined using the *TWIN* command on SHELXL-97 in order only to afford racemic twin crystal. In complexes 3-5, the disordered ClO<sub>4</sub><sup>-</sup> (3), PF<sub>6</sub><sup>-</sup> (4), BF<sub>4</sub><sup>-</sup> (5) anions and MeOH molecules (5) were restrained to the same thermal displacement parameter using the EADP commands on SHELXL-97. The hydrogen atoms of the disordered Me group for complex 2 and OH moiety for complex 3 were not located. The final cycle of full-matrix

least-squares refinement was based on {3920, 3908}, {3420, 3070}, {4212, 3882}, and {4141, 3900} observed reflections (all data,  $I > 2\sigma(I)$ ) for complexes 2-5, respectively. The un-weighted and weighted agreement factors of  $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ ,  $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$  ( $F_o > 4\sigma(F_o)$ ), and  $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)]^{1/2}$  were used. The  $R$ ,  $R_1$ , and  $wR_2$  values were {0.0273, 0.0272, and 0.0723}, {0.0574, 0.0494, and 0.1293}, {0.0639, 0.0567, and 0.1231} and {0.0442, 0.0420, and 0.1179} for complexes 2-5, respectively. All calculations were performed using WinGX 1.80. Crystal data and details of the structure determination are summarized in Table 1.

## Results and discussion

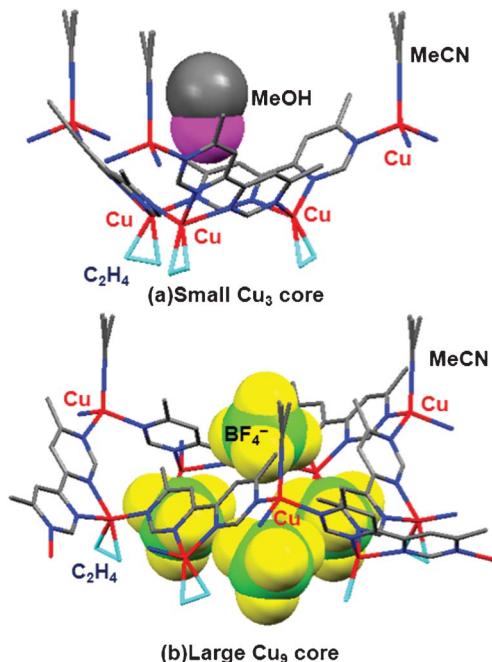
### Crystal structures of Cu(I)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes

**[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(MeCN)](BF<sub>4</sub>)<sub>4</sub>·0.33MeOH** (2). The reaction of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> with Me<sub>2</sub>bpm in MeOH under C<sub>2</sub>H<sub>4</sub> afforded brick crystals of complex 2. The crystal structure of Cu(I)-Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>-BF<sub>4</sub> complex 2 is shown in Fig. 1. Each Cu atom is coordinated by three N atoms in chelate and bridging sites of Me<sub>2</sub>bpm and the C=C bond of C<sub>2</sub>H<sub>4</sub> in the distorted tetrahedral geometry. Three Cu atoms are bridged by three Me<sub>2</sub>bpm ligands to form a metallacalix[3]arene structure with three legs of C<sub>2</sub>H<sub>4</sub>. Furthermore, the metallacalix[3]arene structures of the [Cu<sub>3</sub>(Me<sub>2</sub>bpm)<sub>3</sub>]<sup>3+</sup> framework are linked through another Cu atom with the disordered MeCN in the terminal N atom of Me<sub>2</sub>bpm to produce a 2D sheet structure with small Cu<sub>3</sub> and large Cu<sub>9</sub> cavities. This result shows that a 2D sheet Cu(I)-C<sub>2</sub>H<sub>4</sub> adduct can be reasonably produced by the combination of a Cu(I) ion with a BF<sub>4</sub><sup>-</sup> anion and Me<sub>2</sub>bpm in MeOH under C<sub>2</sub>H<sub>4</sub> in a manner similar to the Cu(I)-bpm/C<sub>2</sub>H<sub>4</sub>-BF<sub>4</sub> complex, 1.<sup>4a</sup> Although the 2D sheet framework of complex 2 apparently resembles that of complex 1, the structural difference between Cu(I)-C<sub>2</sub>H<sub>4</sub> adducts 1 and 2 is that discrete metallacalix[3]arene structures are linked through the Cu atom with the disordered MeCN in contrast to the linkages through the Cu atom with the disordered MeOH in complex 1. Another difference is the accommodation manner of the anions and solvents in small Cu<sub>3</sub> and larger Cu<sub>9</sub> cavities. In the small triangular Cu<sub>3</sub> cavity, one MeOH molecule is accommodated in contrast to the encapsulation of one BF<sub>4</sub><sup>-</sup> anion in complex 1. In the large Cu<sub>9</sub> cavity, one BF<sub>4</sub><sup>-</sup> anion is surrounded by six Me groups of three Me<sub>2</sub>bpm on the upside and three BF<sub>4</sub><sup>-</sup> anions are accommodated on the downside in contrast to the encapsulation of three disordered BF<sub>4</sub><sup>-</sup> anions in complex 1. Consequently, the crystal packing structure of complex 2 is different from that of complex 1: the crystallographic lattice constant was changed from hexagonal *P*6<sub>3</sub> (complex 1) to trigonal *R*3 (complex 2) and the *c*-axis length is elongated (15.2145(16) Å for 1, and 22.6054(6) Å for 2). As shown in Fig. 2, the repeating unit of four-layered 2D sheet structures is arranged in parallel along the *c*-axis in the unit cell in contrast to that of three-layered 2D sheet structures in complex 1. It is suggested that these structural differences were probably caused by the steric effect of the Me group in the Me<sub>2</sub>bpm ligand. In the coordinated C<sub>2</sub>H<sub>4</sub> of complex 2, the C=C distance of 1.340(6) Å is slightly longer than that [1.313 (exptl.) and 1.333 (calc.) Å] in the metal-free C<sub>2</sub>H<sub>4</sub><sup>8</sup> as well as that (1.31(2) Å) in complex 1.<sup>4a</sup>

**Table 1** Crystallographic data of Cu(i)-Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes **2–5**

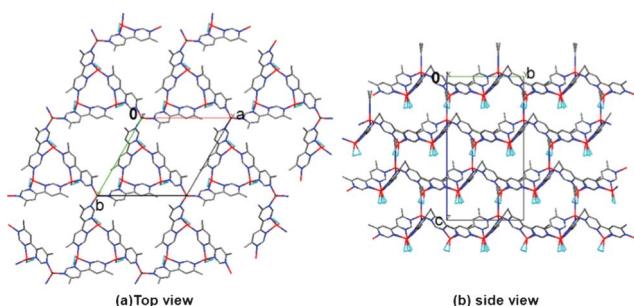
	{[Cu <sub>4</sub> (Me <sub>2</sub> bpm) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> (MeCN)]- (BF <sub>4</sub> ) <sub>4</sub> ·0.33MeOH} <sub>n</sub> ( <b>2</b> )	{[Cu <sub>4</sub> (Me <sub>2</sub> bpm) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> - (MeOH) <sub>0.33</sub> ](ClO <sub>4</sub> ) <sub>4</sub> } <sub>n</sub> ( <b>3</b> )	{[Cu <sub>4</sub> (Me <sub>2</sub> bpm) <sub>3</sub> (CO) <sub>3</sub> (MeCN)]- (PF <sub>6</sub> ) <sub>4</sub> ·0.33MeCN} <sub>n</sub> ( <b>4</b> )	[Cu <sub>4</sub> (Me <sub>2</sub> bpm) <sub>4</sub> (CO) <sub>4</sub> ]- (BF <sub>4</sub> ) <sub>4</sub> ·4MeOH ( <b>5</b> )
Formula	C <sub>38.32</sub> H <sub>43.32</sub> B <sub>4</sub> Cu <sub>4</sub> F <sub>16</sub> N <sub>13</sub> O <sub>0.33</sub>	C <sub>36.33</sub> H <sub>42</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>12</sub> O <sub>16.33</sub>	C <sub>37</sub> H <sub>30</sub> Cu <sub>4</sub> F <sub>24</sub> N <sub>14</sub> O <sub>3</sub> P <sub>4</sub>	C <sub>48</sub> H <sub>56</sub> B <sub>4</sub> Cu <sub>4</sub> F <sub>16</sub> N <sub>16</sub> O <sub>8</sub>
Formula weight	1292.74	1304.06	1552.79	1586.49
Crystal system	Trigonal	Trigonal	Trigonal	Tetragonal
Space Group	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	<i>I</i> 42d
<i>a</i> Å	14.0511(8)	14.448(14)	14.3797(15)	12.9479(9)
<i>b</i> Å	14.0511(8)	14.448(14)	14.3797(15)	12.9479(9)
<i>c</i> Å	22.6054(16)	21.25(2)	23.083(3)	40.274(3)
$\alpha$ (°)	90.0	90.0	90.0	90.0
$\beta$ (°)	90.0	90.0	90.0	90.0
$\gamma$ (°)	120.0	120.0	120.0	90.0
<i>V</i> /Å <sup>3</sup>	3865.1(4)	3841(6)	4133.6(8)	6751.9(8)
<i>Z</i>	3	3	3	4
<i>D</i> <sub>calc</sub> /gcm <sup>-3</sup>	1.666	1.700	1.871	1.561
<i>F</i> (000)	1966	1976	2298	3200
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	17.33	19.26	17.72	13.47
<i>T</i> /K	130(2)	119(2)	120(2)	120(1)
Observed reflections	14 763 ( <i>R</i> <sub>int</sub> = 0.0232)	9878 ( <i>R</i> <sub>int</sub> = 0.0385)	10 806 ( <i>R</i> <sub>int</sub> = 0.0401)	20 146 ( <i>R</i> <sub>int</sub> = 0.0245)
Refined reflections	3920 (all data); 3908 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3420 (all data); 3070 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4212 (all data); 3882 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4141 (all data); 3900 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
<i>R</i>	0.0273 (all data)	0.0574 (all data)	0.0639 (all data)	0.0442 (all data)
<i>R</i> <sub>1</sub>	0.0272 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0494 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0567 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0420 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
wR <sub>2</sub>	0.0723 (all data)	0.1293 (all data)	0.1231 (all data)	0.1179 (all data)
GOF	1.106	1.122	1.076	1.046

$R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ .  $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$  ( $F_o > 4\sigma(F_o)$ ).  $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)]^{1/2}$ .



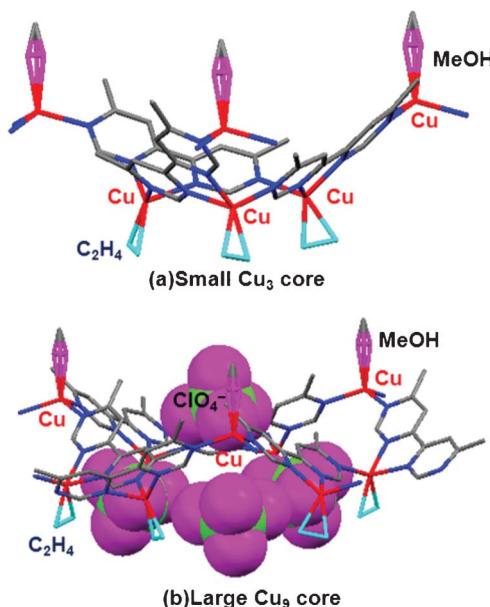
**Fig. 1** X-ray structures of complex **2** encapsulating one MeOH molecule in the small Cu<sub>3</sub> cavity (a) and four BF<sub>4</sub><sup>-</sup> anions in the large Cu<sub>9</sub> cavity (b).

{[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(MeOH)<sub>0.33</sub>](ClO<sub>4</sub>)<sub>4</sub>}<sub>n</sub> (**3**). A similar reaction of [Cu(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>]ClO<sub>4</sub> with Me<sub>2</sub>bpm in MeOH under C<sub>2</sub>H<sub>4</sub> gave red plate crystals of complex **3**. The X-ray crystal structures of Cu(i)-Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>-ClO<sub>4</sub> complex **3** are shown in Fig. 3. The crystal packing structures are deposited in Fig. S1 as ESI.† The metallacalix[3]arene structures of [Cu<sub>3</sub>(Me<sub>2</sub>bpm)<sub>3</sub>]<sup>3+</sup> framework with three legs of C<sub>2</sub>H<sub>4</sub> are linked through another Cu



**Fig. 2** X-ray crystal packing structures of complex **2** along the *c* (a) and *a*-axis (b). The encapsulating MeOH and BF<sub>4</sub><sup>-</sup> anions were omitted for clarity.

atom with the disordered MeOH in the terminal N atom of Me<sub>2</sub>bpm to produce a 2D sheet structure with small Cu<sub>3</sub> and large Cu<sub>9</sub> cavities. The repeating unit of four-layered 2D sheet structures is arranged in parallel along the *c*-axis in the unit cell. Although the 2D sheet structure of complex **3** is therefore similar to that of Cu(i)-Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>-BF<sub>4</sub> adduct **2**, the structural difference between Cu(i)-Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub> adducts **2** and **3** is that the metallacalix[3]arene structures of [Cu<sub>3</sub>(Me<sub>2</sub>bpm)<sub>3</sub>]<sup>3+</sup> are linked through the Cu atom with the disordered MeOH in contrast to the linkages through the Cu atom with the disordered MeCN in complex **2**. It should be noted that the small triangular Cu<sub>3</sub> cavities with neighbouring Cu···Cu distances of 6.12 Å are empty. In the large Cu<sub>9</sub> cavity, one ClO<sub>4</sub><sup>-</sup> anion is surrounded by six Me groups on the upside and three disordered ClO<sub>4</sub><sup>-</sup> anions are accommodated on the downside. There have been few reports about the encapsulation of a ClO<sub>4</sub><sup>-</sup> anion into macrocycles and cages.<sup>9</sup> This result shows that the ClO<sub>4</sub><sup>-</sup> anion can serve as anion templates in the formation of a 2D sheet Cu(i) C<sub>2</sub>H<sub>4</sub> adduct while accompanying a remarkable solvent-dependent effect since the similar reaction

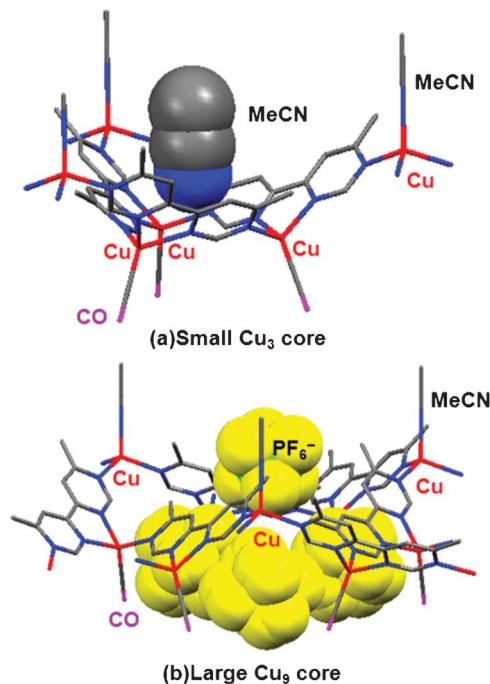


**Fig. 3** X-ray structures of complex 3 encapsulating four  $\text{ClO}_4^-$  anions in the large  $\text{Cu}_9$  cavity (b) and the vacant small  $\text{Cu}_3$  cavity (a).

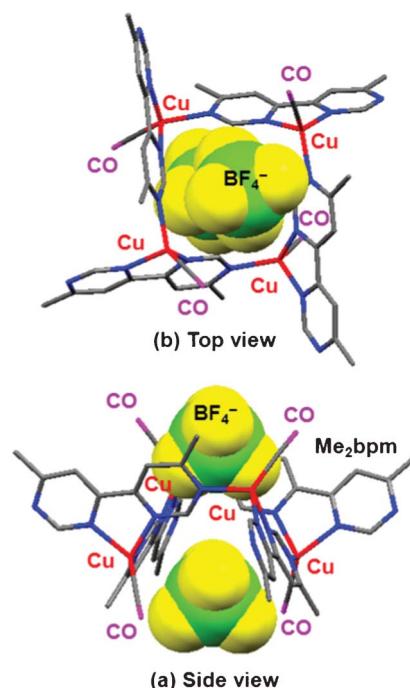
of  $[\text{Cu}(\text{C}_2\text{H}_4)_2]\text{ClO}_4$  with bpm in  $\text{Me}_2\text{CO}$  under  $\text{C}_2\text{H}_4$  afforded a 1D ladder  $\text{Cu}(\text{i})\text{-bpm/C}_2\text{H}_4\text{-ClO}_4$  adduct  $[\{\text{Cu}_3(\text{bpm})_2(\text{C}_2\text{H}_4)_2\}(\text{ClO}_4)_3]_n$ .<sup>4a</sup> Based on the experimental facts in  $\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  adducts 1–3, it was concluded that the reactions of  $\text{Cu}(\text{i})$  ion with  $\{\text{BF}_4^-\}$  or  $\{\text{ClO}_4^-\}$  anions and the related bpm ligands in  $\text{MeOH}$  under  $\text{C}_2\text{H}_4$  preferentially can produce 2D sheet  $\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  adducts. In the coordinated  $\text{C}_2\text{H}_4$ , the  $\text{C}=\text{C}$  distance of  $1.323(10)$  Å is similar to those (1.31(2) for 1; 1.340(6) Å for 2) of related

$\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  adducts 1 and 2. The  $\text{C}=\text{C}$  distance is within those (1.30(1)–1.366(6) Å) in the tetrahedral  $\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  complexes<sup>5b,j</sup> and related  $\text{Cu}(\text{i})\text{-bpm/C}_2\text{H}_4\text{-BF}_4$  complex 1.<sup>4a</sup>

$\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3(\text{CO})_3(\text{MeCN})](\text{PF}_6)_4\cdot0.33\text{MeCN}\}_n$  (4). Further attempts to react  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  with  $\text{Me}_2\text{bpm}$  in  $\text{MeOH}$  under  $\text{CO}$  afforded dark reddish-brown crystals of complex 4. The X-ray crystal structures of  $\text{Cu}(\text{i})\text{-Me}_2\text{bpm/CO-PF}_6$  complex 4 are shown in Fig. 4. The crystal packing structures of complex 4 are deposited in Fig. S2, ESI.† Each Cu atom is coordinated by three N atoms in chelate and bridging sites of  $\text{Me}_2\text{bpm}$  and one CO molecule in the distorted tetrahedral geometry. Three Cu atoms are bridged by three  $\text{Me}_2\text{bpm}$  ligands to form a metallacalix[3]arene structure with three legs of CO. These metallacalix[3]arene structures are linked through another Cu atom with the disordered MeCN in the terminal N atom of  $\text{Me}_2\text{bpm}$  to produce a 2D sheet structure with small  $\text{Cu}_3$  and large  $\text{Cu}_9$  cavities. This result indicates that the preparative approach established in  $\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  adducts 1–3 can apply equally to the self-assembly of the targeted 2D sheet  $\text{Cu}(\text{i})\text{-CO}$  adduct. Contrary to  $\text{Cu}(\text{i})\text{-C}_2\text{H}_4$  adducts 1–3, the structural feature of  $\text{Cu}(\text{i})\text{-CO}$  adduct 4 is that metallacalix[3]arene structures of  $[\text{Cu}_3(\text{Me}_2\text{bpm})_3]^{3+}$  are joined through the Cu atom with the disordered MeCN. Additionally, one MeCN molecule is accommodated in the small triangular  $\text{Cu}_3$  cavities with neighbouring  $\text{Cu}\cdots\text{Cu}$  distances of 5.98 Å. One  $\text{PF}_6^-$  anion is surrounded by six Me groups on the upside and three disordered  $\text{PF}_6^-$  anions are encapsulated on the downside in the large  $\text{Cu}_9$  cavities. There have been few reports about the encapsulation of the  $\text{PF}_6^-$  anion into macrocycles and cages.<sup>9a,10</sup> In the coordinated CO, the CO molecule is coordinative to the Cu(i) atom approximately linearly at the  $\text{Cu}-\text{C}-\text{O}$  angle of  $179.8(9)^\circ$ . The  $\text{C}=\text{O}$  distance of  $1.129(9)$  Å is close to that



**Fig. 4** X-ray structures of complex 4 encapsulating one  $\text{MeCN}$  molecule in the small  $\text{Cu}_3$  cavity (a) and four  $\text{PF}_6^-$  anions in the large  $\text{Cu}_9$  cavity (b).



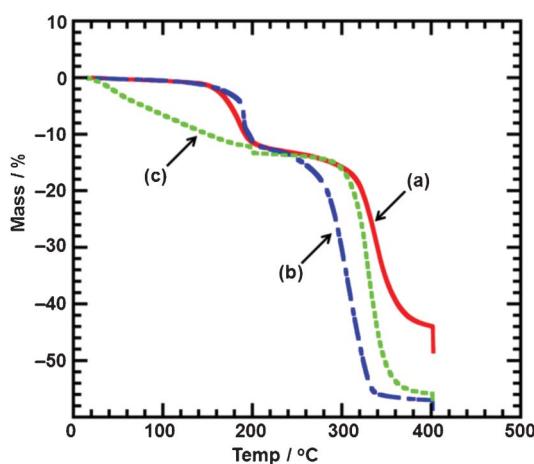
**Fig. 5** X-ray structures of complex 5 encapsulating two  $\text{BF}_4^-$  anions in the  $\text{Cu}_4$  cavity. Side (a) and top views (b).

(1.13 Å) of the metal-free CO and those (1.113(5)–1.128(5) Å) in tetrahedral Cu(I)–CO complexes with three N-donor atoms.<sup>4c,11</sup>

**[Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>4</sub>(CO)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub>·4MeOH (5).** In contrast to polymeric Cu(I)–Me<sub>2</sub>bpm/CO–PF<sub>6</sub> adduct **4**, the similar reaction of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> with Me<sub>2</sub>bpm in MeOH under CO afforded yellowish-brown crystals of complex **5**. The crystal structure of Cu(I)–Me<sub>2</sub>bpm/CO–BF<sub>4</sub> complex **5** is shown in Fig. 5. Each Cu atom is coordinated by three N atoms in the chelating and bridging sites of Me<sub>2</sub>bpm and one CO molecule in the distorted tetrahedral geometry. Four Cu atoms are bridged by four Me<sub>2</sub>bpm to form a metallamacrocyclic tetranuclear structure. One N atom of the bridging sites in the Me<sub>2</sub>bpm ligand is coordinatively unsaturated. Two of the four BF<sub>4</sub><sup>–</sup> anions are functionally accommodated in the upper and lower cavities of the [Cu<sub>4</sub>(Me<sub>2</sub>bpm)<sub>4</sub>] framework, enhancing the stabilization of metallamacrocycles.<sup>4a,c,d</sup> Therefore, the structure of Cu(I)–Me<sub>2</sub>bpm/CO adduct **5** is largely different from those of the expected 2D Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts **2–4**. This result is suggested that the anion sizes and shapes were significantly recognized as a template in the formation process of Cu(I)–Me<sub>2</sub>bpm/CO adducts: the smaller tetrahedral BF<sub>4</sub><sup>–</sup> anion preferentially can induce metallamacrocyclic Cu(I)–Me<sub>2</sub>bpm/CO adduct **5** and the larger octahedral PF<sub>6</sub><sup>–</sup> anion can produce 2D sheet Cu(I)–Me<sub>2</sub>bpm/CO adduct **4**. The encapsulations of the BF<sub>4</sub><sup>–</sup> anion into macrocycles and cage compounds have been limited.<sup>4a,4d,9a,9b,10a,12</sup> In the coordinated CO, the Cu–C–O angle of 175.8(6)° is slightly bent. The C≡O distance of 1.092(6) Å is shorter than that (1.13 Å) of the metal-free CO as well as those (1.113(5)–1.128(5) Å) in tetrahedral Cu(I)–CO complexes with three N-donor atoms.<sup>4c,11</sup>

#### TG-DTA curves, variable-temperature XRPD spectra, and IR spectra of Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes

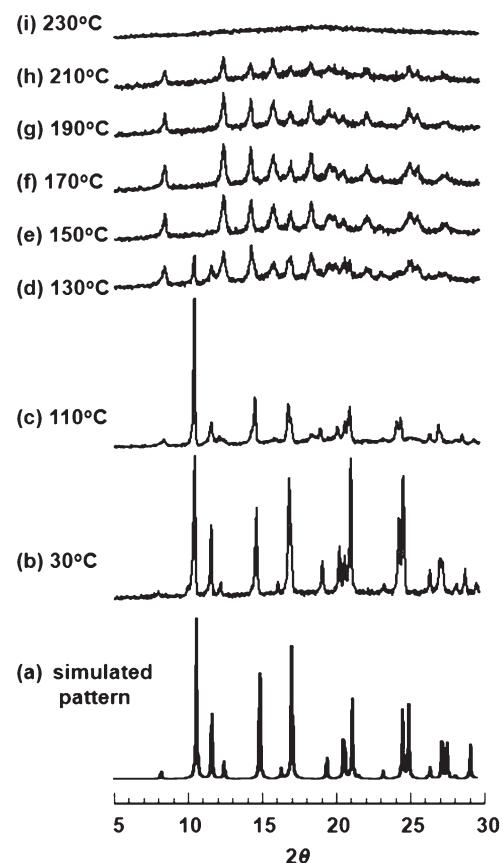
Thermogravimetric analysis (TG-DTA) was carried out under 20 ml min<sup>–1</sup> flowing N<sub>2</sub> gas for Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} complexes **2**, **4**, and **5** except for the explosive Cu(I)–Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>–ClO<sub>4</sub> complex **3**. The temperature was ramped at a rate of 5° min<sup>–1</sup> from 20 to 400 °C. As shown in Fig. 6, the 2D sheet



**Fig. 6** TG-DTA curves of complexes **2**, **4** and **5** under flowing N<sub>2</sub> gas. Solid line (a) for complex **2**, dashed-dotted line (b) for complex **4** and broken line (c) for complex **5**.

Cu(I)–Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>–BF<sub>4</sub> complex **2** displayed a mass loss of two-step curves at 20–205 °C (sharp, 11.9%) and 205–400 °C (sharp, 32.3%). The mass loss of 11.9% at the first step is correlated with the elimination of three C<sub>2</sub>H<sub>4</sub>, 0.33 MeOH and one CH<sub>3</sub>CN molecules (calcd. 10.5%). The sharp curve with distinct steps suggests that complex **2** became more thermochemically stable, in comparison to the gentle curve of the related Cu(I)–bpm/C<sub>2</sub>H<sub>4</sub>–BF<sub>4</sub> complex **1**.<sup>4a</sup> The 2D sheet Cu(I)–Me<sub>2</sub>bpm/CO–PF<sub>6</sub> adduct **4** showed a mass loss of two-step curves at 20–205 °C (sharp, 11.9%) and 205–360 °C (sharp, 44.6%). The mass loss of 11.9% at the first step is correlated with the elimination of three CO and two CH<sub>3</sub>CN molecules (calcd. 10.7%). In contrast, tetranuclear Cu(I)–Me<sub>2</sub>bpm/CO–BF<sub>4</sub> adduct **5** showed a mass loss of two-step curves at 20–205 °C (gentle, 13.4%) and 205–400 (sharp, 42.7%). The mass loss of 13.4% at the first step is correlated with the elimination of four CO and four H<sub>2</sub>O molecules (calcd. 12.0%).

To determine the thermochemical stability of Cu(I)–Me<sub>2</sub>bpm/{C<sub>2</sub>H<sub>4</sub>, CO} adducts, the variable-temperature XRPD spectra of Cu(I)–Me<sub>2</sub>bpm/C<sub>2</sub>H<sub>4</sub>–BF<sub>4</sub> complex **2** were representatively measured with respect to each 20 °C at a rate of temperature increase of 10° min<sup>–1</sup> from 30 to 290 °C (Fig. 7). The measured diffraction pattern of complex **2** is very consistent with the simulated pattern. The X-ray diffraction intensity revealed that the original diffraction pattern was changed to another diffraction pattern at 110–130 °C, and subsequently the crystalline



**Fig. 7** The simulated XRPD pattern (a) and variable-temperature XRPD spectra (b)–(i) with respect to each 20 °C in 30–290 °C of complex **2**.

disappeared at 210–230 °C. This result shows that the 2D sheet framework of the  $\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3](\text{BF}_4)_4\}_n$  moiety should be maintained up to around 200 °C with the elimination of the coordinated  $\text{C}_2\text{H}_4$  and  $\text{CH}_3\text{CN}$  molecules and the solvated  $\text{MeOH}$  molecules, although it is now difficult to describe the detailed structural changes by the elimination of individual molecules. This consideration is very consistent with the suggestions obtained from the TG-DTA curves.

The  $\nu_{\text{C}=\text{C}}$  bands of  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4$  adducts **2** and **3** are observed at 1542 and 1543  $\text{cm}^{-1}$  [metal-free  $\text{C}_2\text{H}_4$ , 1623  $\text{cm}^{-1}$ ]; these values are close to that (1545  $\text{cm}^{-1}$ ) of the related  $\text{Cu}(\text{i})\text{--bpm}/\text{C}_2\text{H}_4$  complex **1**.<sup>4a</sup> In contrast, the  $\nu_{\text{C}=\text{O}}$  bands of  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{CO}$  adducts **4** and **5** appear at 2126 and 2110  $\text{cm}^{-1}$  [metal-free  $\text{CO}$ , 2143  $\text{cm}^{-1}$ ]; these values are higher than those (2063–2119  $\text{cm}^{-1}$ ) in cationic and neutral tetrahedral  $\text{Cu}(\text{i})\text{--CO}$  complexes with three N-donor atoms.<sup>5i,11a,b,d,e</sup>

## Conclusion

As summarized in Scheme 1, the reaction of the  $\text{Cu}(\text{i})$  ion with a  $\text{BF}_4^-$  anion and  $\text{Me}_2\text{bpm}$  instead of bpm in  $\text{MeOH}$  under  $\text{C}_2\text{H}_4$  afforded the 2D sheet  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4\text{--BF}_4$  complex **2** with small  $\text{Cu}_3$  and larger  $\text{Cu}_9$  cavities. It was proved that a 2D sheet  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4$  adduct can be reasonably produced by the combination of a  $\text{Cu}(\text{i})$  ion with a  $\text{BF}_4^-$  anion and  $\text{Me}_2\text{bpm}$  in a manner similar to  $\text{Cu}(\text{i})\text{--bpm}/\text{C}_2\text{H}_4\text{--BF}_4$  complex **1**.<sup>4a</sup> Although the 2D sheet framework apparently resembles  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adducts **1** and **2**, the accommodation manner of anions and solvents in complex **2** is different from that of complex **1**: the repeating unit of four-layered 2D sheet structures is arranged in parallel along the *c*-axis in the unit cell. It is suggested that these structural differences were probably caused by the steric effect of the Me group in the  $\text{Me}_2\text{bpm}$  ligand. The reaction of  $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$  with  $\text{Me}_2\text{bpm}$  in  $\text{MeOH}$  under  $\text{C}_2\text{H}_4$  gave the similar 2D sheet  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4\text{--ClO}_4$  complex **3** with small  $\text{Cu}_3$  cavities and large  $\text{Cu}_9$  cavities. It is proved that the  $\text{ClO}_4^-$  anion can serve as anion templates in the formation of a 2D sheet  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adduct with accompanying a remarkable solvent-dependent effect since the similar reaction of  $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$  with bpm in  $\text{Me}_2\text{CO}$  under  $\text{C}_2\text{H}_4$  afforded a 1D ladder  $\text{Cu}(\text{i})\text{--bpm}/\text{C}_2\text{H}_4\text{--ClO}_4$  adduct.<sup>4a</sup> Based on the experimental facts in  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adducts **1–3**, it was concluded that the reactions of a  $\text{Cu}(\text{i})$  ion with  $\{\text{BF}_4^-\}$  or  $\{\text{ClO}_4^-\}$  anions and the related bpm ligands in  $\text{MeOH}$  under  $\text{C}_2\text{H}_4$  preferentially can produce 2D sheet  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adducts under the direction of anions and solvents. As a further investigation, we attempted to self-assemble a targeted 2D sheet  $\text{Cu}(\text{i})\text{--CO}$  adduct by the applications of a preparative approach established in 2D sheet  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adducts. The reactions of  $[\text{Cu}(\text{MeCN})_4]\text{X}$  ( $\text{X} = \text{PF}_6^-$  or  $\text{BF}_4^-$ ) with  $\text{Me}_2\text{bpm}$  in  $\text{MeOH}$  under  $\text{CO}$  anion-selectively afforded the 2D sheet  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{CO}\text{--PF}_6$  complex **4** and the metallamacrocyclic tetranuclear  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{CO}\text{--BF}_4$  complex **5**. It was confirmed that the anion sizes and shapes

were significantly recognized as a template in the formation process of  $\text{Cu}(\text{i})\text{--Me}_2\text{bpm}/\text{CO}$  adducts. These new findings are expected to contribute to the design and architecture of not only the few 2D sheet  $\text{Cu}(\text{i})\text{--C}_2\text{H}_4$  adducts but also structural and functional new inorganic anion receptors, in combination with previous results regarding the related  $\text{Cu}(\text{i})\text{--}\{\text{pprd, bpm}\}/\text{C}_2\text{H}_4$  complexes.<sup>4</sup>

## Acknowledgements

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## References

- (a) D. H. Busch, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1992, **12**, 389; (b) F. Diederich, P. J. Stang, *Templates Organic Synthesis*, Wiley-VCH, Weinheim, 2000; (c) C. A. Schalley, F. Voegtle and K. H. Doetz, *Templates in Chemistry I. Top Curr Chem.*, 2005, 248; (d) C. A. Schalley, F. Voegtle and K. H. Doetz, *Templates in Chemistry II. Top Curr Chem.*, 2005, 249.
- (a) A. Bianchi, K. Bowman-James, E. García-España, *Supramolecular Chemistry of Anions*, Wiley-VCH, Weinheim, 1997; (b) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181; (c) P. D. Beer and P. A. Gale, *Angew. Chem. Int. Ed.*, 2001, **40**, 486; (d) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79; (e) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191; (f) R. Vilar, *Angew. Chem. Int. Ed.*, 2003, **42**, 1460; (g) N. Gimeno and R. Vilar, *Coord. Chem. Rev.*, 2006, **250**, 3161; (h) R. Vilar, *Struct. Bonding*, 2008, **129**, 175; (i) R. Vilar, *Eur. J. Inorg. Chem.*, 2008, 357; (j) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520.
- D. A. Beauchamp and S. J. Loeb, *Dalton Trans.*, 2007, 4760.
- (a) M. Maekawa, T. Tominaga, K. Sugimoto, T. Okubo, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *CrystEngComm*, 2012, **14**, 1345; (b) M. Maekawa, T. Tominaga, T. Okubo, T. Kuroda-Sowa and M. Munakata, *Eur. J. Inorg. Chem.*, 2009, 4225; (c) M. Maekawa, H. Konaka, T. Minematsu, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *Chem. Commun.*, 2007, 5179; (d) M. Maekawa, A. Nabe, T. Tominaga, K. Sugimoto, T. Minematsu, T. Okubo, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *Dalton Trans.*, 2009, 415.
- (a) H. V. R. Dias and J. Wu, *Eur. J. Inorg. Chem.*, 2008, 509; (b) J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522; (c) J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, 1984, **23**, 2813; (d) H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa and M. Munakata, *J. Organomet. Chem.*, 1987, **322**, 121; (e) M. Munakata, T. Kuroda-Sowa, M. Maekawa and M. Nakamura, *Inorg. Chem.*, 1994, **33**, 1284; (f) J. Dai, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and M. Munakata, *Inorg. Chem.*, 1997, **36**, 2688; (g) Y. Suenaga, L.-P. Wu, T. Kuroda-Sowa, M. Munakata and M. Maekawa, *Polyhedron*, 1997, **16**, 67; (h) B. F. Straub, F. Eisenträger and P. Hofmann, *Chem. Commun.*, 1999, 2507; (i) X. Dai and T. H. Warren, *Chem. Commun.*, 2001, 1998; (j) H. V. R. Dias, H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browning and C. J. Lovely, *Organometallics*, 2002, **21**, 1466; (k) H. V. R. Dias, X. Wang and H. V. K. Diyabalanage, *Inorg. Chem.*, 2005, **44**, 7322; (l) H. V. R. Dias, S. Singh and J. A. Flores, *Inorg. Chem.*, 2006, **45**, 8859; (m) G. Santiso-Quinones, A. Reisinger, J. Slattery and I. Krossing, *Chem. Commun.*, 2007, 5046; (n) J. A. Flores and H. V. R. Dias, *Inorg. Chem.*, 2008, **47**, 4448; (o) M. J. Bainbridge, J. R. L. Smith and P. H. Walton, *Dalton Trans.*, 2009, 3143; (p) J. A. Flores, V. Badarinarayana, S. Singh, C. J. Lovely and H. V. R. Dias, *Dalton Trans.*, 2009, 7648; (q) X. Kou and H. V. R. Dias, *Dalton Trans.*, 2009, 7529; (r) C. Martin, J. M. Munoz-Molina, A. Locati, E. Alvarez, F. Maseras, T. R. Belderrain and P. J. Perez, *Organometallics*, 2010, **29**, 3489.
- G. J. Gubus, *Inorg. Synth.*, 1979, **19**, 90.
- E. Ioachim, E. A. Medlycott, M. I. J. Polson and G. S. Hanan, *Eur. J. Org. Chem.*, 2005, 3775.

8 (a) G. J. H. v. Nes and A. Vos, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **B35**, 2593; (b) I. Krossing and A. Reisinger, *Angew. Chem. Int. Ed.*, 2003, **42**, 5725 and references cited therein.

9 (a) R.-D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem. Int. Ed.*, 1999, **38**, 168; (b) X.-T. Meng, Q.-S. Li, F.-B. Xu, H.-B. Song, C. E. Anson and Z.-Z. Zhang, *Inorg. Chem.*, 2006, **45**, 7986; (c) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 12909.

10 (a) R.-D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381; (b) D. A. McMorran and P. J. Steel, *Angew. Chem. Int. Ed.*, 1998, **37**, 3295.

11 (a) K. Singh, J. R. Long and P. Stavropoulos, *Inorg. Chem.*, 1998, **37**, 1073; (b) R. R. Conry, G. Ji and A. A. Tipton, *Inorg. Chem.*, 1999, **38**, 906; (c) A. J. Blake, D. A. Carling, M. W. George, P. Hubberstey, R. L. Garcia and C. Wilson, *Acta Cryst. C*, 2002, **E58**, m41; (d) M. Costas, R. Xifra, A. Llobet, M. S. J. Robles, T. Parella, H. Stoeckli-Evans and M. Neuburger, *Inorg. Chem.*, 2003, **42**, 4456; (e) H. V. R. Dias and T. K. H. H. Goh, *Polyhedron*, 2004, **23**, 273.

12 (a) S. Mann, G. Huttner, L. Zsolnai and K. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2808; (b) M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1997, **119**, 6324; (c) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Angew. Chem. Int. Ed.*, 1998, **37**, 1279; (d) C. S. Campos-Fernández, R. Clerac and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 1999, **38**, 3477; (e) H. Amouri, M. N. Rager, F. Cagnol and J. Vaissermann, *Angew. Chem. Int. Ed.*, 2001, **40**, 3636; (f) H. Amouri, L. Mimassi, M. N. Rager, B. E. Mann, C. Guyard-Duhayon and L. Raehm, *Angew. Chem. Int. Ed.*, 2005, **44**, 4543; (g) S. P. Argent, H. Adams, T. Riis-Johannessen, J. C. Jeffery, L. P. Harding, O. Mamula and M. D. Ward, *Inorg. Chem.*, 2006, **45**, 3905.