CrystEngComm

Cite this: *CrystEngComm*, 2012, **14**, 1345

www.rsc.org/crystengcomm

PAPER

Framework dimensionality of copper(I) coordination polymers of 4,4′-bipyrimidine controlled by anions and solvents†

Masahiko Maekawa,*[a] Toshi Tominaga,[b] Kunihisa Sugimoto,[c] Takashi Okubo,[b] Takayoshi Kuroda-Sowa,[b] Megumu Munakata[b] and Susumu Kitagawa[d]

Received 7th October 2011, Accepted 9th November 2011
DOI: 10.1039/c1ce06328f

The reaction of $[Cu(C_2H_4)_n]NO_3$ with 4,4′-bipyrimidine (bpm) in Me_2CO under C_2H_4 afforded a polymeric Cu(I)–bpm/C_2H_4 adduct $[Cu_2(bpm)(C_2H_4)(NO_3)_2]_n$ (**1**) with an infinite 1-D zigzag chain structure. Similar reactions of $[Cu(C_2H_4)_n]ClO_4$ or $[Cu(MeCN)_4]BF_4$ with bpm in Me_2CO under C_2H_4 afforded Cu(I)–bpm/C_2H_4 adducts $\{[Cu_3(bpm)_2(C_2H_4)_2](ClO_4)_3\}_n$ (**2**) and $\{[Cu_3(bpm)_2(C_2H_4)_2]–(BF_4)_3\}_n$ (**3**), respectively, which have an infinite 1-D zigzag ladder structure. It is interesting that two disordered ClO_4^- or BF_4^- anions are accommodated in the inside cavity of the ladder chains. In contrast, the reaction of $[Cu(MeCN)_4]BF_4$ with bpm in MeOH under C_2H_4 afforded a Cu(I)–bpm/C_2H_4 adduct $\{[Cu_4(bpm)_3(C_2H_4)_3(MeOH)](BF_4)_4\cdot 2H_2O\cdot 3MeOH\}_n$ (**4**). Three Cu atoms are bridged by three bpm ligands to form a metallacalix[3]arene structure with three legs of C_2H_4. Furthermore, these metallacalix[3]arenes are linked through another Cu atom in the terminal N atom of bpm to produce a chiral 2-D sheet structure with space group $P6_3$. One BF_4^- anion is accommodated in the small triangular Cu_3 cavities, whereas three disordered BF_4^- anions are encapsulated in the large triangular Cu_3 cavities. In contrast to complex **4**, $[Cu(MeCN)_4]BF_4$ was reacted with bpm in MeOH under Ar, and C_2H_4 gas was then bubbled into the resultant brown suspensions. The reaction solution was allowed to come to room temperature, and Cu(I)–bpm complex $\{[Cu_3(bpm)_3](SiF_6)_{1.5}\}_n$ (**5**) was collected. The tetrahedral Cu atom is coordinated by two N atoms in the chelate site of bpm and two N atoms in the terminal sites of two other bpm ligands to form two racemic metallacalix[3]arene structures. It is noteworthy that these metallacalix[3]arenes are joined through the bpm ligands to afford a 3-D cage structure consisting of two right-handed and left-handed helix networks. One disordered SiF_6^{2-} anion is accommodated in the inside cavity between two opposite metallacalix[3]arene structures. On the basis of these results, it has been concluded that BF_4^-, PF_6^-, ClO_4^- and SiF_6^{2-} anions can serve as anion templates to self-assemble polymeric Cu(I) C_2H_4 adducts and a cage compound in complexes **2–5**. The NO_3^- anion is ineffective as an anion template, as indicated by the higher coordination ability of the NO_3^- anion in complex **1**. Additionally, solvent-dependent effects have been observed in the formation process: Me_2CO can preferentially induce polymeric 1-D chain and 1-D ladder structures in complexes **1–3**, whereas MeOH can produce 2-D sheet and 3-D cage structures by the linkage of metallacalix[3]–arene structures in complexes **4** and **5**.

Introduction

The rational design of inorganic artificial receptors for host–guest chemistry is one of the most attractive areas in contemporary supramolecular chemistry.[1] In particular, metal-assembled bowl-shaped molecules that are structural analogues of calixarenes and cyclotriveratrylenes have attracted considerable attention,[2] in contrast to their versatile behaviours as hosts for inclusion complexation and as efficient ligands for metal ions in classical calixarenes.[3] A successful strategy for forming metallamacrocycles closely related to calixarenes has been developed by the combination of *cis*-protected d^8 metal units such as Pd(II) or Pt(II) and an appropriate *N*-heterocyclic ligand such as

[a]*Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan. E-mail: maekawa@rist.kindai.ac.jp*
[b]*Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan*
[c]*Research and Utilization Division, Japan Synchrotron Radiation Research Institute, Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan*
[d]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan*

† Electronic supplementary information (ESI) available: The SEM images and CD spectrum for complex **4** are given in Fig. S1 and S2. CCDC reference numbers 829823, 829824, 829825, 803344 and 803345 for complexes **1–5**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce06328f

pyrimidine or 4,7-phenanthroline derivatives. Recently, a new approach utilizing anion templation to construct metallamacrocycles and cages has been employed with several reported successes.[4] However, in contrast to the well-studied templating properties of cationic and neutral species, the use of anionic components to direct the self-assembly process is an area of supramolecular chemistry still in its infancy.

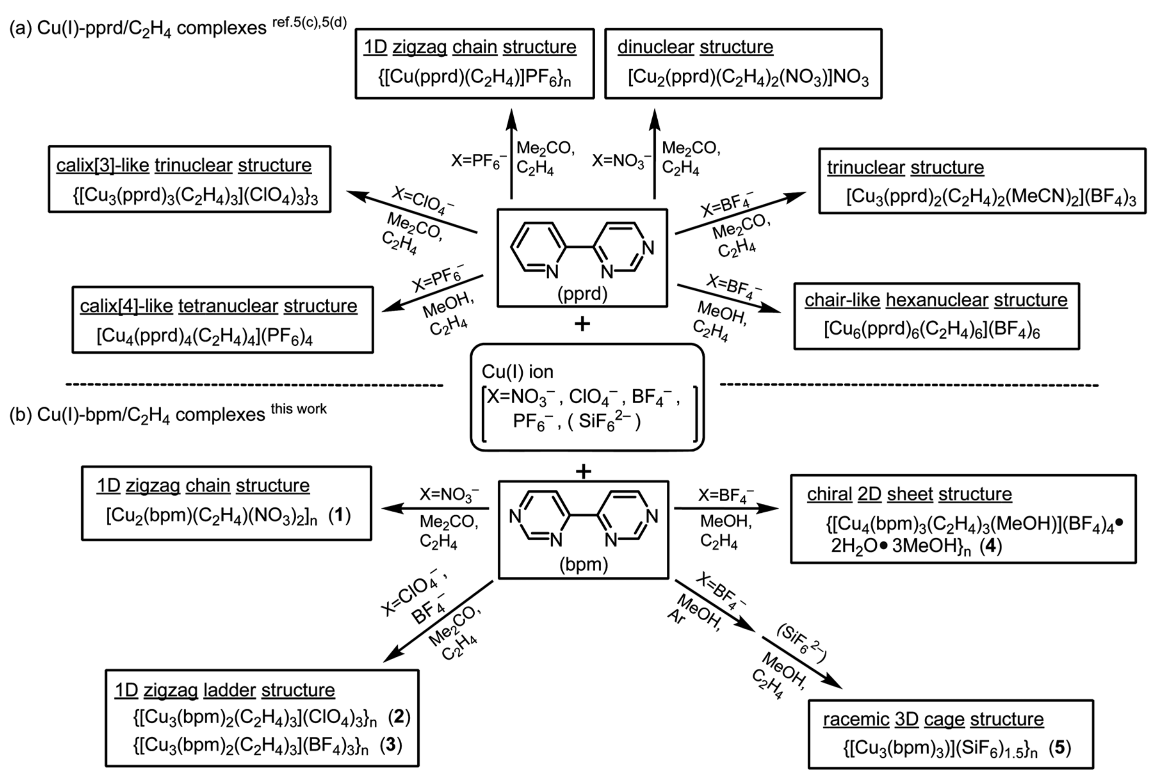
The 4-(2-pyridyl)pyrimidine (pprd) ligand is an attractive nitrogen ligand with a bidentate site for chelation and an *exo* *N*-donor site for bridging.[5] We have adopted the combination of a Cu(I) or Ag(I) ion and the pprd ligand to construct novel bowl-shaped metallamacrocycles. It has been shown that Cu(I)–pprd metallamacrocycles with C_2H_4 and CO legs encapsulating ClO_4^-, PF_6^- and BF_4^- anions can be self-assembled by the controls of anion and solvent (Scheme 1(a)),[5c,d] together with sandwich-shaped Ag(I)–pprd metallamacrocycles encapsulating XF_6^{2-} (X = Si, Ge and Sn) anions.[5b] Similar to the pprd ligand, 4,4′-bipyrimidine (bpm) possesses 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. It is expected to produce a greater diversity of finite metallamacrocyclic and infinite polymeric compounds with square/rectangle motifs. However, only a few preliminary reports of the coordination polymers of Cu(I),[6] Ag(I)[6b,7] and Rh(III)[8] with bpm and derivatives can be found in the literature. Using 6,6′-diphenyl-4,4′-bipyrimidine (Ph_2bpm) as a bpm derivative, we have recently reported that diverse 3-D Cu(I)–Ph_2bpm/C_2H_4 adducts can be self-assembled by the different connectivities of an intermolecular π–π stacking interaction and a C–H···N contact.[6c]

As a further investigation, we attempted herein to join discrete Cu(I) metallamacrocycles by the combination of Cu(I) ion and bpm ligand and to synthesize a few polymeric Cu(I) C_2H_4 adducts by the application of preparative approach in the related Cu(I)–pprd metallamacrocycles.[5c,d] It was found that a diversity of 1-D chain, 1-D ladder, 2-D sheet Cu(I)–bpm/C_2H_4 adducts and 3-D Cu(I)–bpm cage compound, in which a ClO_4^-, BF_4^- or SiF_6^{2-} anion was accommodated in the inside cavity, could be self-assembled by the controls of anions and solvents (Scheme 1(b)). Their structures and properties were characterized by X-ray, IR, TG-DTA, SEM and CD analyses. The roles of anion and solvent were determined in their formation processes.

Experimental section

General procedures and reagents

$[Cu(MeCN)_4]X$ (X = PF_6 and BF_4) were prepared according to the literature.[9] 4,4′-Bipyrimidine (bpm) was prepared by modifications of the literature method.[10] $Cu(ClO_4)_2·6H_2O$ and $Cu(NO_3)_2·3H_2O$ were purchased from Mitsuwa Chemicals and Wako pure Chemicals, respectively. The pure C_2H_4 gas (>99.9%) was 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 Ar and C_2H_4. 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_2 gas.



Scheme 1 Cu(I)–{pprd, bpm}/C_2H_4 complexes.

Preparation of Cu(I)–bpm complexes

$[Cu_2(bpm)(C_2H_4)(NO_3)_2]_n$ (1). The precursor Cu(I) C_2H_4 complex $[Cu(C_2H_4)_n]NO_3$ was prepared by the reductive reaction of $Cu(NO_3)_2\cdot 3H_2O$ (24.2 mg, 0.10 mmol) with Cu wire in Me_2CO (5 ml) under C_2H_4. A 5 ml Me_2CO solution of bpm (3.2 mg, 0.02 mmol) was added to the Cu(I) C_2H_4 solution. The C_2H_4 gas was then bubbled for 1 hour. The brown suspension was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand at −10 °C for 1 month, and the solution was then allowed to come to room temperature. The brown plate crystals of complex **1** were collected. After complex **1** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis, IR and TG-DTA. Anal. Calcd for $Cu_2C_{10}H_{10}N_6O_6$: C, 27.46; H, 2.30; N, 19.22. Found: C, 27.85; H, 3.17; N, 21.77%. IR (KBr, cm^{-1}): 1636(w), 1601(m), 1577(s), 1559(m, C_2H_4), 1542(w), 1522(m), 1443(m), 1385(s, NO_3), 1183(w), 1155(w), 1060(w), 845(w), 746(m), 692(w), 652(m).

$\{[Cu_3(bpm)_2(C_2H_4)_2](ClO_4)_3\}_n$ (2). The precursor Cu(I) C_2H_4 complex $[Cu(C_2H_4)_n]ClO_4$ was prepared by the reductive reaction of $Cu(ClO_4)_2\cdot 6H_2O$ (37.1 mg, 0.10 mmol) with Cu wire in Me_2CO (5 ml) under C_2H_4. A 5 ml Me_2CO solution of bpm (3.2 mg, 0.02 mmol) was added to the Cu(I) C_2H_4 solution. The C_2H_4 gas was then bubbled for 1 hour. The brown suspension was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand at −10 °C for 1 month, and red plate crystals of complex **2** were collected. After complex **2** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis and IR. Anal. Calcd for $Cu_3C_{20}H_{20}N_8Cl_3O_{12}$: C, 27.89; H, 2.34; N, 13.01. Found: C, 26.26; H, 2.50; N, 11.50%. IR (KBr, cm^{-1}) 1598(s), 1568(s), 1548 (m, C_2H_4), 1536(w), 1474(s), 1396(s), 1335(m, C_2H_4), 1274(w), 1167(s), 1094–927(s, ClO_4), 858(s), 739(s), 684(w), 670(m), 622(s).

Caution: perchlorate salts of metal complexes with organic compounds are potentially explosive! Only small amounts of materials should be prepared and should be handled with great care.

$\{[Cu_3(bpm)_2(C_2H_4)_2](BF_4)_3\}_n$ (3). $[Cu(MeCN)_4]BF_4$ (62.8 mg, 0.20 mmol) and bpm (3.2 mg, 0.02 mmol) were reacted in Me_2CO (10 ml) under C_2H_4. The yellow reaction solution was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand for 2 months at −10 °C, and the solution was then allowed to come to room temperature. The red plate crystals of complex **3** were collected. After complex **3** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis, IR and TG-DTA. Anal. Calcd for $Cu_3C_{20}H_{20}B_3F_{12}N_8$: C, 29.17; H, 2.45; N, 13.61. Found: C, 28.95; H, 2.57; N, 13.53%. IR (KBr, cm^{-1}): 1599(s), 1569(s), 1550(m, C_2H_4), 1476(s), 1409(s), 1338(m, C_2H_4), 1286 (w), 1273(m), 1167(s), 1088–956(s, BF_4), 862(m), 740(s), 685(m), 672(m), 520(m).

$\{[Cu_4(bpm)_3(C_2H_4)_3(MeOH)](BF_4)_4\cdot 2H_2O\cdot 3MeOH\}_n$ (4). $[Cu(MeCN)_4]BF_4$ (62.8 mg, 0.20 mmol) and bpm (3.2 mg, 0.02 mmol) were reacted in MeOH (10 ml) under C_2H_4. The yellow reaction solution was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand for 1 week at −10 °C. Two kinds of reddish-brown hexagonal prismatic (**4a**) and plate crystals (**4b**) were collected. The preliminary X-ray determinations showed that both crystals had the same crystallographic lattice constants. A single crystal X-ray analysis was carried out using appropriate plate crystals **4b**. After complex **4** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis, IR and TG-DTA. Anal. Calcd for $Cu_4C_{34}H_{50}N_{12}O_6B_4F_{16}$: C, 30.84; H, 3.81; N, 12.69. Found: C, 30.70; H, 3.75; N, 12.63%. IR (KBr, cm^{-1}): 1596(s), 1568(m), 1545(m, C_2H_4), 1472(s), 1402(s), 1335(m, C_2H_4), 1285(m) 1167(s), 1062(s, BF_4), 843(m), 742(s), 696(w), 685(w), 666(s), 521(m).

$\{[Cu_3(bpm)_3](SiF_6)_{1.5}\}_n$ (5). $[Cu(MeCN)_4]BF_4$ (9.4 mg, 0.03 mmol) and bpm (1.6 mg, 0.01 mmol) were reacted in MeOH (10 ml) under Ar. The C_2H_4 gas was bubbled into dark brown suspensions to form a clear yellow solution. The reaction solution was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand for 1 month at −10 °C, and the solution was then allowed to come to room temperature. The black brick crystals of complex **5** were collected after 2 weeks. After complex **5** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis and IR. Anal. Calcd for $Cu_3C_{24}H_{18}N_{12}Si_{1.5}F_9$: C, 32.82; H, 2.07; N, 19.14; Found: C, 32.65; H, 2.03; N, 19.04%. IR (KBr, cm^{-1}): 1637(w), 1577(s), 1523(m), 1444(m), 1384(s), 1277(w), 1184(m), 1084(m), 1061(m), 845(m), 747(s, SiF_6), 484(s, SiF_6), 450(w).

X-ray crystal structure determinations

All measurements of Cu(I)–bpm complexes **1–5** were made on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71070 Å). The diffraction data were collected at −157(2), −165(2), −153(2), −175(2) and −155(2) °C for complexes **1–5** in the ω scan mode, respectively. Of the 10 327, 11 447, 17 589, 32 111 and 35 743 reflections that were collected, 3258, 3651, 3464, 4171 and 1248 were unique (R_{int} = 0.0240, 0.0484, 0.0310, 0.0486 and 0.0523) for complexes **1–5**, respectively. Data were collected and processed using the Crystal Clear program (Rigaku). The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 29.96, 23.47, 21.65, 16.343 and 21.07 cm^{-1} for complexes **1–5**, respectively. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (*SHELXS*-97) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included and constrained to the ideal position and thermal displacement parameter using the AFIX command on *SHELXL*-97. In complex **2**, one of the disordered ClO_4^- anions was restrained as the same thermal displacement parameter using the EADP command on *SHELXL*-97. In complex **3**, fluorine atoms of the disordered BF_4^- anions were restrained for the thermal displacement parameter using the DELU and SIMU commands on *SHELXL*-97. In complex **4b**, each disordered BF_4^- anion, MeOH, and H_2O except boron and hydrogen atoms were restrained to the same thermal displacement parameters using the EADP commands on *SHELXL*-97, respectively. In complex **5**, the disordered F(3) and F(4) atoms of SiF_6^{2-} anions were restrained for thermal displacement parameters using the DELU and SIMU commands on *SHELXL*-97. The hydrogen atoms of disordered water molecules were not located. The final cycle of full-matrix least squares refinement was based on {3258, 2814}, {3651, 2606}, {3464, 2955}, {4171, 4033} and {1248, 1247} observed reflections (all data, $I > 2\sigma(I)$) for complexes **1–5**, respectively. The unweighted 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 $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$ were used. The R, R_1 and wR_2 values were {0.0434, 0.0317 and 0.0686}, {0.0703, 0.0685 and 0.1941}, {0.0703, 0.0685 and 0.1941}, {0.0703, 0.0685 and 0.1941} and {0.0727, 0.0726 and 0.1729} for complexes **1–5**, respectively. All calculations were performed using the *WinGX* 1.80. Crystal data and details of the structure determination are summarized in Table 1.

Results and discussion

Crystal structures of Cu(I)–bpm complexes

$[Cu_2(bpm)(C_2H_4)(NO_3)_2]_n$ (1). The reaction of $[Cu(C_2H_4)_n]$–NO_3 with bpm in Me_2CO under C_2H_4 afforded brown plate crystals of $[Cu_2(bpm)(C_2H_4)(NO_3)_2]_n$ (**1**). The crystal structure of complex **1** is presented in Fig. 1. The Cu atom is coordinated by two N atoms of bpm in the chelate site and the C═C bond of C_2H_4 in a trigonal-planar geometry. The other Cu atom is coordinated by two N atoms of the different bpm ligands in the *exo* bridging site and two O atoms of the different NO_3^- anions in a distorted tetragonal geometry to form an infinite 1-D zigzag

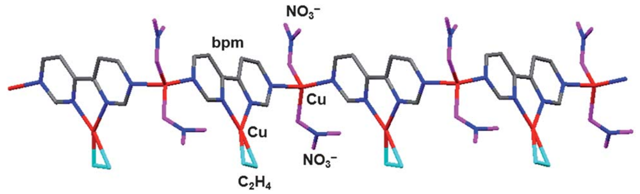


Fig. 1 X-Ray crystal structure of complex **1**.

chain structure. Although there have been several Cu(I) complexes with a NO_3^- anion in the chelating bidentate mode[11] and the bridging bidentate manner,[12] there are few Cu(I) complexes with a NO_3^- anion in the unidentate coordination mode.[5d,11b,d,f] Additionally, Cu(I) C_2H_4 adducts have been poorly characterized due to the extremely labile nature of the Cu(I)–C_2H_4 interaction.[5c,d,6c,13] In particular, preparative and structural reports of polynuclear and polymeric Cu(I) C_2H_4 complexes are few.[5c,d,6c,13e,f] Therefore, polymeric Cu(I)–bpm/C_2H_4 adduct **1** with the η^1-NO_3^- anion is of significance. In our related Cu(I)–pprd complexes (Scheme 1(a)), we have proved that the conformation of metallamacrocyclic Cu(I)–pprd/C_2H_4, CO adducts can be controlled by the choice of anion: the self-assemblies by anion templation of BF_4^-, PF_6^- and ClO_4^- under C_2H_4 preferentially can induce metallamacrocyclic Cu(I)–pprd/C_2H_4, CO adducts.[5c,d] In contrast, the NO_3^- anion is ineffective as an anion template in the formation of expected metallamacrocyclic Cu(I)–pprd/C_2H_4 adducts due to the higher coordination ability of the NO_3^- anion. In fact, the reaction of $[Cu(C_2H_4)_n]NO_3$ with pprd in

Table 1 Crystal data of Cu(I)–bpm complexes **1–5**[a]

	$[Cu_2(bpm)(C_2H_4)$–$(NO_3)_2]_n$ (**1**)	$\{[Cu_3(bpm)_2(C_2H_4)_2]$–$(ClO_4)_3\}_n$ (**2**)	$\{[Cu_3(bpm)_2(C_2H_4)_2]$–$(BF_4)_3\}_n$ (**3**)	$\{[Cu_4(bpm)_3(C_2H_4)_3(MeOH)]$–$(BF_4)_4\cdot 2H_2O\cdot 3MeOH\}_n$ (**4b**)	$\{[Cu_3(bpm)_3](SiF_6)_{1.5}\}_n$ (**5**)
Formula	$C_{10}H_{10}Cu_2N_6O_6$	$C_{20}H_{20}Cl_3Cu_3N_8O_{12}$	$C_{20}H_{20}B_3Cu_3F_{12}N_8$	$C_{34}H_{49}Cu_4N_{12}B_4F_{16}O_6$	$C_{48}H_{36}Cu_6N_{24}Si_3F_{18}$
Formula weight	437.32	861.44	823.49	1323.23	1756.48
Crystal system	Monoclinic	Monoclinic	Monoclinic	Hexagonal	Cubic
Space group	$P2_1/a$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P6_3$ (no. 173)	$Ia3(-)$ (no. 206)
a/Å	14.897(9)	20.8073(9)	20.8286(7)	14.384(5)	18.673(5)
b/Å	5.819(3)	13.2133(18)	12.9965(5)	14.384(5)	18.673(5)
c/Å	17.441(10)	15.3486(11)	15.3593(5)	15.215(5)	18.673(5)
α/°	90.0	90.0	90.0	90.0	90.0
β/°	107.581(6)	132.126(2)	132.5660(10)	90.0	90.0
γ/°	90.0	90.0	90.0	120.0	90.0
V/Å^3	1441.4(14)	3129.7(5)	3062.17(19)	2726.2(16)	6510.9(18)
Z	4	4	4	2	4
D_{calc}/g cm^{-3}	2.015	1.828	1.786	1.498	1.820
F(000)	872.0	1720.0	1624.0	1316.0	3536.0
μ (Mo-Kα)/cm^{-1}	29.96	23.47	21.65	16.343	21.07
Temperature/K	116(2)	108(2)	120(2)	98(2)	118(2)
Observed reflections	10 327 (R_{int} = 0.0237)	11 447 (R_{int} = 0.0484)	17 589 (R_{int} = 0.0310)	32 111 (R_{int} = 0.0486)	35 743 (R_{int} = 0.0523)
Refined reflections	3258 (all data); 2814 ($I > 2\sigma(I)$)	3651 (all data); 2606 ($I > 2\sigma(I)$)	3464 (all data); 2955 ($I > 2\sigma(I)$)	4171 (all data); 4033 ($I > 2\sigma(I)$)	1248 (all data); 1247 ($I > 2\sigma(I)$)
R	0.0434 (all data)	0.0870 (all data)	0.0418 (all data)	0.0703 (all data)	0.0727 (all data)
R_1	0.0317 ($I > 2\sigma(I)$)	0.0570 ($I > 2\sigma(I)$)	0.0326 ($I > 2\sigma(I)$)	0.0685 ($I > 2\sigma(I)$)	0.0726 ($I > 2\sigma(I)$)
wR_2	0.0686 (all data)	0.1475 (all data)	0.0761 (all data)	0.1941 (all data)	0.1729
GOF	1.099	1.067	1.057	1.074	1.422
Flack parameter	—	—	—	0.07(3)	—

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

Me_2CO under C_2H_4 afforded dinuclear Cu(I)–pprd/C_2H_4 complex, $[Cu_2(pprd)(C_2H_4)_2(NO_3)]NO_3$.[5d] In this study, two NO_3^- anions were similarly coordinated to the Cu atom in the terminal bridging sites of bpm in the η^1-fashion. This finding suggests that the NO_3^- anion is ineffective as an anion template in the construction of expected metallamacrocyclic Cu(I)–bpm/C_2H_4 adducts, although the combination of $[Cu(C_2H_4)_n]NO_3$ and bpm under C_2H_4 can produce a rare polymeric 1-D zigzag chain Cu(I) C_2H_4 adduct. In the coordinated C_2H_4, the C=C distance of 1.373(4) Å is slightly longer than those [1.30(1)–1.366(6) Å] in the reported trigonal-planar Cu(I) C_2H_4 complexes[5d,13c–i] and that [1.313 (exptl) and 1.333 (calc.) Å] of metal-free C_2H_4.[14] The average Cu–N distance of 2.011 Å in the terminal bridging site is slightly shorter than that (2.006 Å) in the chelate site.

$\{[Cu_3(bpm)_2(C_2H_4)_2](ClO_4)_3\}_n$ (2) and $\{[Cu_3(bpm)_2(C_2H_4)_2]-(BF_4)_3\}_n$ (3). The reaction of $[Cu(C_2H_4)_n]ClO_4$ with bpm in Me_2CO under C_2H_4 afforded red plate crystals of $\{[Cu_3(bpm)_2-(C_2H_4)_2](ClO_4)_3\}_n$ (**2**). In contrast to complex **1**, this result indicates a significant anion-dependent effect in the formation process of Cu(I)–bpm/C_2H_4 adducts. The crystal structure of complex **2** is shown in Fig. 2. The Cu atom is coordinated by four N atoms in the chelate site of two different bpm ligands in the distorted tetrahedral geometry. The other Cu atom is coordinated by two terminal N atoms in the bridging sites of two different bpm ligands and the C=C bond of C_2H_4 in the distorted trigonal geometry to form an infinite 1-D zigzag ladder structure. It is interesting that two disordered ClO_4^- anions are accommodated in the inside cavity of the ladder chains. Although there have been several reports of the encapsulation of NO_3^-,[15] BF_4^-,[5d,15a,b,16] PF_6^-,[15a,b,17] Cl_2[18] and I_2^{2-}[19] anions, less is known about the encapsulation of a ClO_4^- anion into macrocycles and cages.[15a,16h,20]

A similar reaction of $[Cu(MeCN)_4]BF_4$ with bpm in Me_2CO under C_2H_4 gave red plate crystals of $\{[Cu_3(bpm)_2(C_2H_4)_2]-(BF_4)_3\}_n$ (**3**). The crystal structure of complex **3** is shown in Fig. 3. The infinite 1-D zigzag ladder structure of complex **3** essentially resembles that of complex **2**, in which two disordered BF_4^- anions are accommodated in the inside cavity of the ladder chains. These findings indicate that BF_4^- and ClO_4^- anions can serve as anion templates in the formation of polymeric 1-D ladder Cu(I) C_2H_4 adducts, although BF_4^- and ClO_4^- anions contribute to the formation of metallamacrocyclic Cu(I) C_2H_4 adducts in the related Cu(I)–pprd complexes.[5c,d]

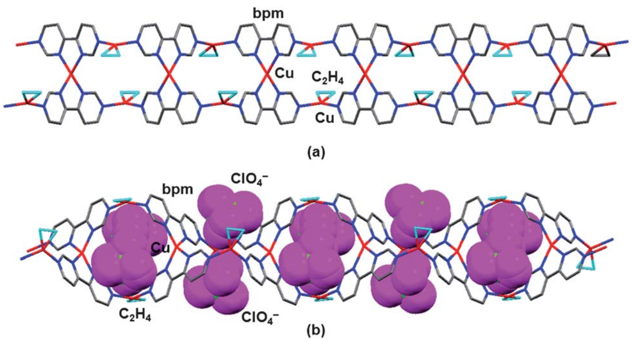


Fig. 2 X-Ray crystal structure of complex **2** encapsulating ClO_4^- anions.

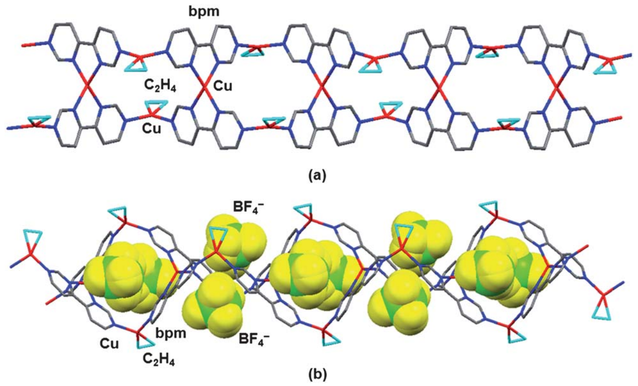


Fig. 3 X-Ray crystal structure of complex **3** encapsulating BF_4^- anions.

In the coordinated C_2H_4, the C=C distances of 1.385(8) and 1.370(9) Å in complexes **2** and **3** are slightly longer than that [1.313 (exptl) and 1.333 (calc.) Å] of the metal-free C_2H_4[14] and those (1.30(1)–1.366(6) Å) in tetrahedral Cu(I) C_2H_4 complexes[13b,j] and related Cu(I)–pprd/C_2H_4 metallamacrocycles.[5c,d]

$\{[Cu_4(bpm)_3(C_2H_4)_3(MeOH)](BF_4)_4\cdot 2H_2O\cdot 3MeOH\}_n$ (4). Further attempts to react $[Cu(MeCN)_4]BF_4$ with bpm in MeOH under C_2H_4 afforded reddish-brown hexagonal prismatic (**4a**) and plate crystals (**4b**) of $\{[Cu_4(bpm)_3(C_2H_4)_3(MeOH)]-(BF_4)_4\cdot 2H_2O\cdot 3MeOH\}_n$, with the crystals of both having the same crystallographic lattice constants. In contrast to complex **3**, this result indicates a remarkable solvent-dependent effect in the formation process of Cu(I)–bpm/C_2H_4 adducts. The SEM images of crystals **4a** and **4b** are shown in Fig. 4. In particular, it is interesting that the shape of crystals **4a** showed a hexagonal prismatic structure with a hollow hole, in which the outside diameter is about 250 ± 25 μm and the inside diameter is about 130 ± 10 μm. Although it is difficult to decide the crystal growth process at this time, it is considered that a horn-like shape should be formed by the aggregations of the torus-shape plates according to the enlarged SEM images (ESI, Fig. S1†). For instance, it has been known that the hexagonal $ZnP(Py)_4$ nanorods with a hollow hole could encapsulate fullerene (C_{60}), which showed photo-induced electron transfer and light energy conversion properties.[21] Thus coordination polymers with a hollow hole are expected to develop into structurally and functionally interesting host compounds.

A single crystal X-ray analysis was carried out using appropriate plate crystals **4b**. The crystal structure of complex **4b** is

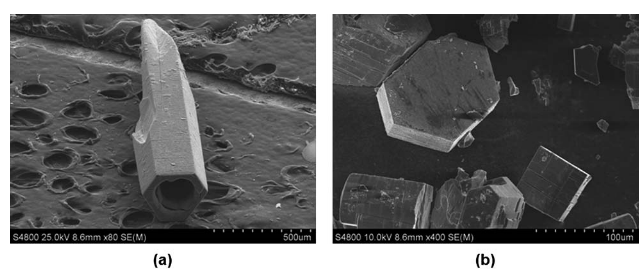


Fig. 4 The SEM images of hexagonal prismatic crystals for **4a** (a) and plate crystals for **4b** (b).

shown in Fig. 5. No inversion center was found, confirming $P6_3$ as the correct space group. Each Cu atom is coordinated by three N atoms in chelate and bridging sites of bpm and the C=C bond of C_2H_4 in the distorted tetrahedral geometry. Three Cu atoms are bridged by three bpm ligands to form a metallacalix[3]arene structure with three legs of C_2H_4. Furthermore, these metallacalix[3]arenes are linked through another Cu atom with MeOH in the terminal N atom of bpm to produce a 2-D sheet structure with small and large Cu_3 cavities (Fig. 5). Although C_2H_4 adducts to the 2-D surfaces of $CuMCl_4$ (M = Al and Ga) have been determined by powder X-ray diffraction analysis,[22] complex **4b** is the first 2-D sheet Cu(I) C_2H_4 adduct. It should be noted that each 2-D sheet structure is arranged in parallel along the *c*-axis, resulting in the formation of a chiral 2-D sheet structure (Fig. 6 and 7). The presence of chirality could be confirmed by circular dichroic (CD) spectroscopy in the solid state (ESI, Fig. S2†). The positive cotton effect was observed. More noteworthy are one BF_4^- anion is functionally accommodated in the small triangular Cu_3 cavities with neighbouring Cu···Cu distances of 6.06 Å and three disordered BF_4^- anions are encapsulated in the large triangular Cu_3 cavities with corresponding distances of 14.38 Å. It was shown that the BF_4^- anion can play a role as an anion template to build a chiral 2-D sheet structure consisting of the linkage of $[Cu_3(bpm)_3]$ frameworks with a metallacalix[3]arene structure. To the best of our knowledge, the encapsulations of BF_4^- anion into macrocycles and cage compounds have been limited.[5d,15a,b,16] As such, this compound is expected to develop as an unprecedented inorganic anion receptor with chirality. In the coordinated C_2H_4, the C=C distance of 1.31(2) Å is similar to that [1.313 (exptl) and 1.333 (calc.) Å] of the metal-free C_2H_4[14] and those (1.30(1)–1.366(6) Å) in tetrahedral Cu(I) C_2H_4 complexes[13b,j] and related Cu(I)–pprd/C_2H_4 metallamacrocycles.[5c,d] The average Cu–N distance of 2.025 Å in the terminal bridging site is slightly shorter than that (2.144 Å) in the chelate site.

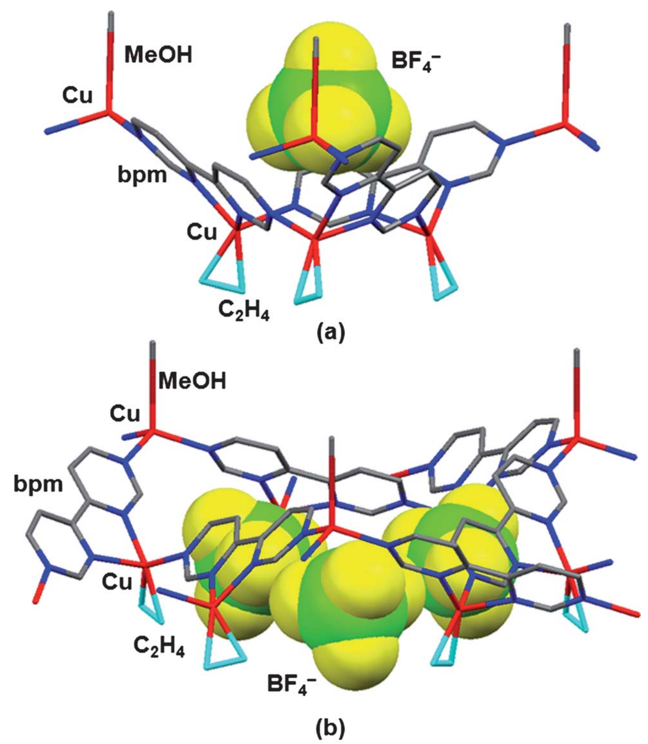


Fig. 5 X-Ray crystal structure of complex **4b** encapsulating BF_4^- anions in small (a) and large Cu_3 cavities (b).

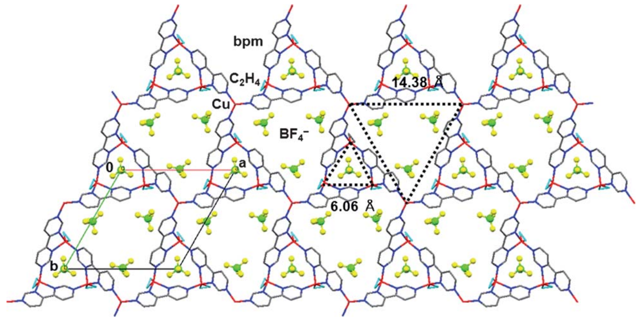


Fig. 6 2-D sheet structure of complex **4b** encapsulating BF_4^- anions. The solvated MeOH and H_2O molecules are omitted for clarity.

$\{[Cu_3(bpm)_3](SiF_6)_{1.5}\}_n$ (5). In contrast to Cu(I) C_2H_4 adduct **4**, $[Cu(MeCN)_4]BF_4$ was reacted with bpm in MeOH under Ar, and the C_2H_4 gas was then bubbled into the resultant brown suspensions to afford a clear yellow solution. The reaction solution was allowed to stand for 2 months at −10 °C, but we were not able to obtain any crystals and precipitates due to the higher solubility. The reaction solution was then allowed to come to room temperature, and black brick crystals of $\{[Cu_3(bpm)_3]-(SiF_6)_{1.5}\}_n$ (**5**) were collected after 2 weeks. The crystal structure of complex **5** is shown in Fig. 8. The tetrahedral Cu atom is coordinated by two N atoms in the chelate site of bpm and two N atoms in the terminal sites of two other bpm ligands to form two racemic metallacalix[3]arene structures, in which the neighbouring triangular Cu···Cu distances are 5.73 Å. It is noteworthy that these metallacalix[3]arenes are joined through the bpm ligands to afford a 3-D cage structure consisting of two right-handed (blue) and left-handed (red) helix networks. One disordered SiF_6^{2-} anion is accommodated in the inside cavity between two opposite metallacalix[3]arene structures (Fig. 9). Although

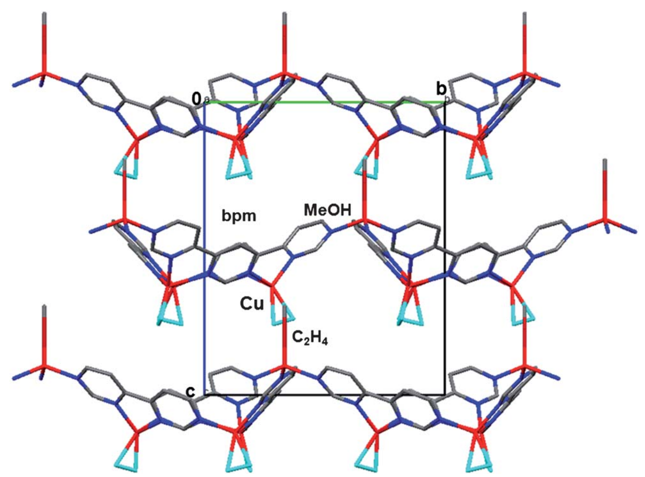


Fig. 7 X-Ray crystal packing structure of complex **4b** along the *a*-axis. The solvated MeOH and H_2O molecules are omitted for clarity.

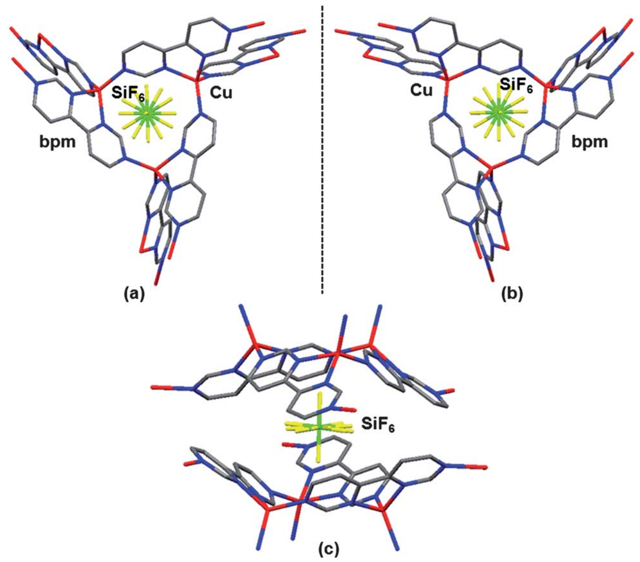


Fig. 8 X-Ray crystal structures of complex **5** encapsulating disordered SiF_6^{2-} anions. Top {(a) and (b)} and side views (c) in two racemic metallacalix[3]arene structures.

there have been only a few reports regarding the encapsulation of a SiF_6^{2-} anion to create sandwich-shaped Ag(I) metallamacrocycles[5b] and an organic anion complex,[23] the encapsulation of a SiF_6^{2-} anion into a racemic 3-D Cu(I) cage compound is quite unique. It would be interesting to elucidate the formation process of this 3-D Cu(I) cage compound. Presumably, a chopped Cu(I)–bpm/C_2H_4 complex should be induced from a polymeric Cu(I)–bpm complex by the addition of C_2H_4 since a dark brown suspension under Ar was changed to a clear yellowish-brown solution upon bubbling of C_2H_4. Similar behaviors have been observed in the formation process of our related Cu(I)–pprd/C_2H_4 adducts.[5c] Subsequently, a coordinatively unsaturated Cu(I)–bpm complex would be produced as an intermediate in the dissociation equilibrium of C_2H_4 upon the reaction solution standing at room temperature. Finally, the SiF_6^{2-} anion could act as an anion template to form a 3-D Cu(I) cage compound **5**.[5b] These results also suggest that a source of SiF_6^{2-} anion can be introduced by the reaction of a BF_4^- anion and SiO_2 component from a glass-made reactor and tube.[5b,23,24]

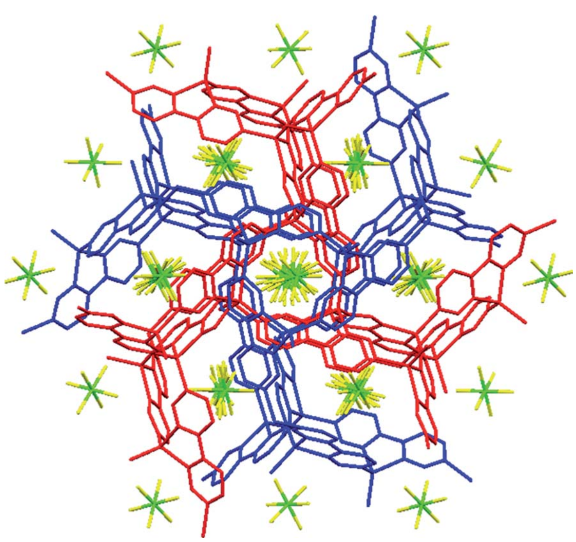


Fig. 9 3-D Cu(I) cage structure of complex **5** encapsulating disordered SiF_6^{2-} anions, which consist of two right-handed (blue) and left-handed (red) helix networks.

TG-DTA curves and IR spectra of Cu(I)–bpm/C_2H_4 adducts

Thermogravimetric analysis (TG-DTA) was carried out under 20 ml min^{-1} flowing N_2 gas for Cu(I)–bpm/C_2H_4 adducts **1**, **3** and **4** except for explosive Cu(I)–bpm/C_2H_4–ClO_4 complex **2**. The temperature was ramped at a rate of 5° min^{-1} from 20 to 400 °C. As shown in Fig. 10, 1-D chain Cu(I)–bpm/C_2H_4 adduct **1** displayed a mass loss of three-step curves at 20–115 (sharp, 7.2%), 115–185 (gentle, 1.6%) and 185–250 °C (sharp, 36.8%). The thermal decomposition of complex **1** was determined near 250 °C with the rapid mass loss by the elimination of bpm ligands in accordance with exothermic DTA behaviors. The mass loss of 7.2% at the first step is correlated with the elimination of one C_2H_4 molecule (calcd 6.4%). The total mass loss of 38.4% (calcd 36.1%) at the sum of first and second steps was roughly identical to the elimination of one bpm molecule. Similarly, 1-D ladder Cu(I)–bpm/C_2H_4 adducts **3** showed a mass loss of three-step curves at 20–70 (gentle, 6.6%), 70–170 (gentle, 7.5%) and 170–330 °C (sharp, 12.9%). The mass loss of 6.6% at the first step is correlated with the elimination of two C_2H_4 molecules (calcd 6.8%). The total mass loss of 20.4% (calcd 19.2%) at the sum of the first and second steps was roughly assigned to the elimination of one bpm molecule. In contrast, 2-D sheet Cu(I)–bpm/C_2H_4 adducts **4** showed a total mass loss of 20.3% (calcd 18.8%) with gentle relatively unclear three-step curves at 20–120 (10.0%) and 120–320 °C (10.3%) corresponding to three C_2H_4, two H_2O and four MeOH molecules, and the curve subsequently showed a sharp decline from around 320 °C in response to the elimination of the bpm ligand. At the present time, gentle two-step curves are unidentified due to simultaneous desorptions of the coordinated C_2H_4 and MeOH molecules and the solvated H_2O and MeOH

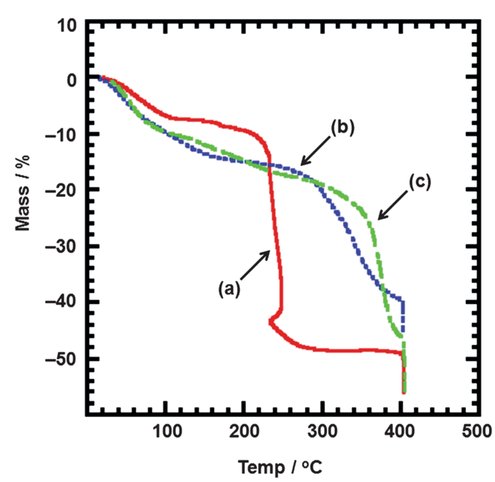


Fig. 10 TG-DTA curves of Cu(I)–bpm/C_2H_4 adducts **1**, **3** and **4** under flowing N_2 gas. Solid line (a) for **1**, broken line (b) for **3** and dashed-dotted line (c) for **4**.

molecules, although endothermic DTA behaviour was clearly observed at the first step (20–120 °C).

The $\nu_{C=C}$ bands of Cu(I)–bpm/C_2H_4 adducts **1–4** are observed at 1559 (**1**), 1548 (**2**), 1550 (**3**) and 1545 (**4**) cm^{-1}, respectively [metal-free C_2H_4, 1623 cm^{-1}]. These $\nu_{C=C}$ wavenumbers are slightly larger than those (1537–1543 cm^{-1}) of the related Cu(I)–pprd/C_2H_4 metallamacrocycles encapsulating ClO_4^-, PF_6^- and BF_4^- anions,[5c,5d] indicative of the contribution of poor Cu → C_2H_4 π back-bonding.

Conclusion

As summarized in Scheme 1, the reactions of Cu(I) ion with NO_3^-, ClO_4^- and BF_4^- anions and bpm under C_2H_4 in Me_2CO afforded Cu(I)–bpm/C_2H_4 adducts **1–3** with infinite 1-D chain and 1-D ladder structures, whereas similar reactions of Cu(I) ion with BF_4^- and SiF_6^{2-} anions and bpm under C_2H_4 in MeOH gave Cu(I) coordination polymers **4** and **5** with 2-D sheet and 3-D cage structures by the linkage of [$Cu_3(bpm)_3$] frameworks with a metallacalix[3]arene structure. It has been shown that BF_4^-, PF_6^-, ClO_4^- and SiF_6^{2-} anions can serve as anion templates to self-assemble polymeric Cu(I) C_2H_4 adducts and a cage compound in complexes **2–5**. The NO_3^- anion is ineffective as an anion template, as indicated by the higher coordination ability of the NO_3^- anion in complex **1**. Additionally, the solvent-dependent effects are clarified in the formation process: Me_2CO preferentially can induce polymeric 1-D chain and 1-D ladder structures in complexes **1–3**, whereas MeOH can produce 2-D sheet and 3-D cage structures by the linkage of metallacalix[3] arene structures in complexes **4** and **5**. These results are expected to contribute to the design and architecture of structurally and functionally new inorganic anion receptors, in combination with previous results regarding the related Cu(I) and Ag(I) pprd complexes.[5b–d]

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (no. 20550069 and 23550085) from the Ministry of Education, Science, Sports, Culture and Technology in Japan.

Notes and references

1 (*a*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, Chichester, 2nd edn, 2009; (*b*) L. R. MacGillivray, *Metal–Organic Frameworks*, ed. L. R. MacGillivray, Wiley & Sons, New Jersey, 2010; (*c*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspective*, Wiley-VCH: Weinheim, 1995; (*d*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*e*) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; (*f*) L. Cronin, *Annu. Rep. Prog. Chem., Sect. A*, 2003, **99**, 289; (*g*) F. Würthner, C.-C. You, C. R. Saha and Moller, *Chem. Soc. Rev.*, 2004, **33**, 133; (*h*) P. Thanasekaran, R.-T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal and K.-L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085.

2 S. Kumar, N. Kaur and H. Singh, *Adv. Heterocycl. Chem.*, 2008, **96**, 123.

3 (*a*) D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, 1998; (*b*) Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens, *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht, 2001; (*c*) D. J. Cram and J. M. Cram, *Container Molecules and their Guests*, Royal Society of Chemistry, Cambridge, 1994.

4 (*a*) A. Bianchi, K. Bowman-James and E. García-España, *Supramolecular Chemistry of Anions*; Wiely-VCH: Weinheim, 1997; (*b*) P. A. Gale, J. L. Sessler and V. Král, *Chem. Commun.*, 1998, 1; (*c*) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181; (*d*) J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, 2001, **34**, 989; (*e*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*f*) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79; (*g*) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191; (*h*) R. Vilar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1460; (*i*) P. D. Beer, M. R. Sambrook and D. Curiel, *Chem. Commun.*, 2006, 2105; (*j*) N. Gimeno and R. Vilar, *Coord. Chem. Rev.*, 2006, **250**, 3161; (*k*) R. Vilar, *Struct. Bonding*, 2008, **129**, 175; (*l*) R. Vilar, *Eur. J. Inorg. Chem.*, 2008, 357; (*m*) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520.

5 (*a*) D. A. Beauchamp and S. J. Loeb, *Chem. Commun.*, 2002, 2484; (*b*) M. Maekawa, S. Kitagawa, T. Kuroda, Sowa and M. Munakata, *Chem. Commun.*, 2006, 2161; (*c*) M. Maekawa, H. Konaka, T. Minemastu, T. Kuroda, Sowa, M. Munakata and S. Kitagawa, *Chem. Commun.*, 2007, 5179; (*d*) M. Maekawa, A. Nabei, T. Tominaga, K. Sugimoto, T. Minematsu, T. Okubo, T. Kuroda, Sowa, M. Munakata and S. Kitagawa, *Dalton Trans.*, 2009, 415.

6 (*a*) F. Bodar, Houillon, T. Humbert, A. Marsura, J.-B. R. de Vains, O. Dusausoy, N. Bouhmaida, N. E. Ghermani and Y. Dusausoy, *Inorg. Chem.*, 1995, **34**, 5205; (*b*) C. Janiak, L. Uehlin, H.-P. Wu, P. Kliifers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121; (*c*) M. Maekawa, T. Tominaga, T. Okubo, T. Kuroda, Sowa and M. Munakata, *Eur. J. Inorg. Chem.*, 2009, 4225.

7 D. A. Beauchamp and S. J. Loeb, *Dalton Trans.*, 2007, 4760.

8 J. E. Redman, N. Feeder, S. J. Teat and J. K. M. Sanders, *Inorg. Chem.*, 2001, **40**, 2486.

9 G. J. Gubus, *Inorganic Syntheses*, ed by D. F. Shriver, Wiley-Interscience, New York, 1979, 19, 90.

10 E. Ioachim, E. A. Medlycott, M. I. J. Polson and G. S. Hanan, *Eur. J. Org. Chem.*, 2005, 3775.

11 (*a*) M. Munakata, S. Kitagawa, N. Ujimaru, M. Nakamura, M. Maekawa and H. Matsuda, *Inorg. Chem.*, 1993, **32**, 826; (*b*) T. Kuroda, Sowa, M. Munakata, H. Matsuda, S. Akiyama and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1995, 2201; (*c*) C. Pettinari, G. G. Lobbia, G. Sclavi and D. Leonesi, *Polyhedron*, 1995, **14**, 1709; (*d*) V. Olijnyk, T. Glowiak and M. Mys'kiv, *J. Chem. Crystallogr.*, 1995, **25**, 621; (*e*) H. Lang, A. del Villar, B. Walfort and G. Rheinwald, *J. Organomet. Chem.*, 2004, **689**, 1464; (*f*) C. Sivasankar, M. Nethaji and A. G. Samuelson, *Inorg. Chem. Commun.*, 2004, **7**, 238; (*g*) S.-M. Chen, C.-Z. Lu, C.-K. Xia, X.-J. Xu and Q.-G. Zhai, *Cryst. Growth Des.*, 2005, **5**, 1485.

12 (*a*) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455; (*b*) R. Yang, K. Lin, Y. Hou, D. Wang and D. Jin, *Polyhedron*, 1997, **16**, 4033; (*c*) J.-P. Lang, H. Kawaguchi and K. Tatsumi, *J. Organomet. Chem.*, 1998, **569**, 109; (*d*) R. Yang, Y. Sun, D. Zhao and L. Guo, *J. Coord. Chem.*, 2003, **56**, 1169.

13 (*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.

14 (*a*) G. J. H. van Nes and A. Vos, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 2593; (*b*) I. Krossing and A. Reisinger, *Angew. Chem., Int. Ed.*, 2003, **42**, 5725, and references cited therein.

15 (*a*) R.-D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem., Int. Ed.*, 1999, **38**, 168; (*b*) R.-D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381; (*c*) S.-H. Li, H.-P. Huang, S.-Y. Yu, Y.-Z. Li, H. Huang, Y. Sei and K. Yamaguchi, *Dalton Trans.*, 2005, 2346.

16 (*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; (*h*) X.-T. Meng, Q.-S. Li, F.-B. Xu, H.-B. Song, C. E. Anson and Z.-Z. Zhang, *Inorg. Chem.*, 2006, **45**, 7986.

17 D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295.

18 (*a*) R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258; (*b*) S.-T. Cheng, E. Doxiadi, R. Vilar, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 2239; (*c*) J. A. Wisner, P. D. Beer, M. G. B. Drew and M. R. Sambrook, *J. Am. Chem. Soc.*, 2002, **124**, 12469.

19 (*a*) Z. Zheng, C. B. Knobler, M. D. Mortimer, G. Kong and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **35**, 1235; (*b*) M. F. Hawthorne and Z. Zheng, *Acc. Chem. Res.*, 1997, **30**, 267.

20 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.

21 T. Hasobe, A. S. D. Sandanayaka, T. Wada and Y. Araki, *Chem. Commun.*, 2008, 3372.

22 (*a*) R. M. Sullivan, H. Liu, D. S. Smith, J. C. Hanson, D. Osterhout, M. Ciraolo, C. P. Grey and J. D. Martin, *J. Am. Chem. Soc.*, 2003, **125**, 11065; (*b*) M. D. Capracotta, R. M. Sullivan and J. D. Martin, *J. Am. Chem. Soc.*, 2006, **128**, 13463.

23 (*a*) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun and G. L. Thomas, *Chem. Commun.*, 2003, 568; (*b*) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun and G. L. Thomas, *Chem. Commun.*, 2003, 1462, addition and correction to ref. 22*a*.

24 (*a*) J. Reedijk, *Comments Inorg. Chem.*, 1982, **1**, 379; (*b*) P. J. van Koningsbruggen, J. G. Haasnoot, R. A. G. de Graaff and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1993, 483; (*c*) G. A. van Albada, O. Roubeau, I. Mutikainen, U. Turpeinen and J. Reedijk, *New J. Chem.*, 2003, **27**, 1693; (*d*) H. Casellas, A. Pevec, B. Kozlevcar, P. Gamez and J. Reedijk, *Polyhedron*, 2005, **24**, 1549.