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ARTICLE TYPE

Open-framework beryllium phosphates with a zeolitic CrB_4 topology and their structural analogues containing 12-ring channels†

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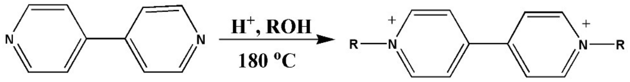
Two new open-framework beryllium phosphates, formulated as $MV\cdot Be_2(HPO_4)_2(H_2PO_4)_2$ (**1**) and $EV\cdot Be_2(HPO_4)_2(H_2PO_4)_2$ (**2**), have been synthesized under solvothermal conditions, where MV = methylviologen, and EV = ethylviologen. The two compounds have large 16-membered ring (16 MR) channels with a zeolitic CrB_4 topology. They contain *in-situ* generated viologen dications from the alkylation of 4,4'-bipyridine (4,4'-bpy) molecules as the structure-directing agents (SDAs). In comparison, the use of 4,4'-bpy and 2,2'-bpy as the SDAs results in the formation of two different open-framework compounds, $(4,4'\text{-}H_2bpy)_2\cdot Be_5(HPO_4)_7$ (**3**) and $(2,2'\text{-}H_2bpy)_{0.5}\cdot Be_3(OH)(HPO_4)_3$ (**4**). Compounds **3** and **4** have different framework structures with 12 MR channels. The presence of large $4^{10}8^{4}12^{4}$ cages in the structure of **3** is noteworthy.

Introduction

Microporous inorganic solids are an important class of solid state materials with potential applications in ion-exchange, gas storage, catalysis, and separation.[1] Zeolite are the most well-known such materials, which contain 4-connected networks built up from corner-sharing TO_4 tetrahedra (T = Si and Al). The discovery of aluminophosphate molecular sieves in 1982 extended crystalline microporous materials to non-aluminosilicate zeotypes, such as metal phosphates, germanates, phosphites, and borates.[2] A notable example is the bimetallic phosphite NTHU-13 with tunable pore sizes ranging from 24-membered ring (24 MR) to 72 MR.[3] From the viewpoint of structural chemistry, beryllium phosphates may represent a suitable system to mimic zeolitic networks because of the tetrahedral coordination geometry of beryllium.[4] During the past years, a number of open-framework beryllium phosphates with zeolitic networks, such as ABW, ANA, BOZ, BPH, CAN, CHA, FAU, GIS, GME, LOS, MER, RHO, SOD, and WEI topologies, have been prepared and structurally characterized.[5] The ring sizes of these zeotypes include 3, 4, 6, 8, 10, and 12 MR.

The use of functional organic cations (e. g., viologens) in the synthesis of new crystalline inorganic-organic hybrid solids is of current interest because of their good electron-accepting ability.[6] Open-framework metal phosphates containing viologen ions may display appealing properties such as photo- or thermo-chromism. For example, the orange color of the zinc phosphate NTHU-9-MV turned to slate gray when it was exposed to X-ray irradiation.[7] The slate gray sample can reverse to orange upon heating at 200 ºC for 10 h. Since this process originates from the charge transfer between the host inorganic framework and guest methylviologen (MV), it is expected that more photochromic compounds may be developed by varying the compositions and structures of host phosphate frameworks. However, with the exception of two open-framework zinc phosphates (i.e., NTHU-9-MV and JU98), we are not aware of any examples of viologen-based metal phosphates.[7, 8] This is in part due to the high cost of viologens from typical commercial suppliers.

In situ template synthesis strategy has shown great potential in the preparation of new open-framework inorganic solids.[9] Several new organic cations were generated within the pores of beryllium phosphates by *in situ* methylation reactions between methanol solvents and amines.[10] The replacement of amines by 4,4'-bipyridine (4,4'-bpy) under similar solvothermal conditions may produce viologen cations as the structure-directing agents (SDAs) (Scheme 1). During the course of such investigation, two new open-framework beryllium phosphates, $MV\cdot Be_2(HPO_4)_2(H_2PO_4)_2$ (**1**) and $EV\cdot Be_2(HPO_4)_2(H_2PO_4)_2$ (**2**), have been successfully isolated, where EV = ethylviologen. Structural analysis reveals that the two compounds have large 16 MR channels with a zeolitic CrB_4 topology. The *in-situ* generated viologen dications are ordered within their intersecting 12 MR, 12 MR, and 16 MR channels. In comparison, the use of 4,4'-bpy and 2,2'-byp as the SDAs results in the formation of two different open-framework beryllium phosphates, namely, $(4,4'\text{-}H_2bpy)_2\cdot Be_5(HPO_4)_7$ (**3**) and $(2,2'\text{-}H_2bpy)_{0.5}\cdot Be_3(OH)(HPO_4)_3$ (**4**). Herein, we report their syntheses, characterizations and crystal structures.



Scheme 1. *In situ* generated viologen dications under solvothermal conditions from the alkylation of 4,4'-bipyridine (ROH = methanol and ethanol).

Experimental

Materials and methods

Reagents were purchased commercially and used without further purification. Powder X-ray diffraction data were collected using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The CHN analyses were carried out on a Euro EA3000 analyzer. IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. The fluorescent spectra were measured on a Perkin-Elmer LS 55 luminescence spectrometer equipped with a 450 W xenon lamp. Powder second-harmonic generation (SHG) signals were measured by means of the Kurtz and Perry method.[11] The fundamental wavelength was 1064 nm and was generated by a Q-switched Nd:YAG laser. The SHG wavelength was 532 nm. KDP powder was used as a reference.

Synthesis of compounds

MV·$Be_2(HPO_4)_2(H_2PO_4)_2$ (1). A mixture of $BeSO_4{\cdot}4H_2O$ (0.089 g), H_3PO_4 (0.115 g, 85 wt%), 4,4'-bipyridine (0.078 g), and methanol (4.0 mL) was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 10 days. The autoclave was subsequently allowed to cool to room temperature. Light-pink crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (33.9 % yield based on beryllium). IR (KBr pellets, cm^{-1}): 3130(w), 3060(w), 1640(m), 1570(w), 1510(w), 1440(w), 1120(s), 833(m), 708(m), 494(m).

EV·$Be_2(HPO_4)_2(H_2PO_4)_2$ (**2**). A mixture of $BeSO_4{\cdot}4H_2O$ (0.177 g), H_3PO_4 (0.230 g, 85 wt%), 4,4'-bipyridine (0.156 g), and ethanol (8.0 mL) was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 9 days. The autoclave was subsequently allowed to cool to room temperature. Colorless crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (87.4 % yield based on beryllium). IR (KBr pellets, cm^{-1}): 3130(w), 3170(w), 1640(m), 1560(w), 1500(w), 1450(w), 1110(s), 829(w), 708(m), 494(m).

(4,4'-H_2bpy)$_2$·$Be_5(HPO_4)_7$ (3). A mixture of $BeSO_4{\cdot}4H_2O$ (0.089 g), H_3PO_4 (0.144 g, 85 wt%), 4,4'-bipyridine (0.078 g), H_2O (1.0 mL), and *n*-butanol (4.0 mL) was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Colorless crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (57.1 % yield based on beryllium). IR (KBr pellets, cm^{-1}): 3090(m), 1620(m), 1490(m), 1120(s), 903(m), 683(m), 492(m).

(2,2-H_2bpy)$_{0.5}$·$Be_3(OH)(HPO_4)_3$ (4). A mixture of $BeSO_4{\cdot}4H_2O$ (0.089 g), H_3PO_4 (0.116 g, 85 wt%), 2,2'-bipyridine (0.156 g), H_2O (0.4 mL), and ethanol (4.0 mL) was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 6 days. The autoclave was subsequently allowed to cool to room temperature. Colorless crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (58.4 % yield based on beryllium). IR (KBr pellets, cm^{-1}): 3390(m), 3160(m), 1640(s), 1320(m), 1080(s), 960(s), 814(w), 600(w), 501(m).

X-Ray crystallography

A suitable single crystal of each compound was carefully selected under an optical microscope and glued to a glass fiber with epoxy resin. Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 diffractometer (for **1**, **2**, **4**) or on an Oxford Xcalibur diffractometer (for **3**) at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL* program package.[12] All non-hydrogen framework atoms were refined anisotropically. The crystallographic data for compounds **1**-**4** are summarized in Table 1. The CCDC reference numbers for **1**-**4** are 1033214 (**1**), 1033215 (**2**), 1033216 (**3**), and 1033217 (**4**), respectively.

Results and discussion

Synthesis and chemical composition

Large single crystals of compounds **1** and **2** were obtained by heating a mixture of $BeSO_4{\cdot}4H_2O$, H_3PO_4, and 4,4'-bpy under different solvothermal conditions. The 4,4'-bpy reacted with methanol or ethanol to generate MV or EV cation as the SDA in the structures of **1** and **2**, respectively. The alkylation of 4,4'-bpy didn't happen when other alcohol molecules (e.g., propanol, isopropyl alcohol, and *n*-butanol) were used as the solvents under similar synthetic conditions. Instead, a new crystalline beryllium phosphate (compound **3**) containing 4,4'-H_2bpy cations as the SDAs was isolated during the course of such investigation. It is also of interest to investigate the structure-directing role of 2,2'-bpy, which has the similar size and shape as 4,4'-bpy. The exploration in the $BeSO_4{\cdot}4H_2O$–H_3PO_4–2,2'-bpy system gave rise to good quality single crystals of compound **4**.

The powder X-ray diffraction pattern of each as-synthesized compound is in good agreement with the simulated one on the basis of single crystal data, indicating the phase purity of as-synthesized compounds (Fig. S1-S4†). CHN elemental analysis confirms the stoichiometry (anal. for **1**: C 24.11 wt%, H 3.38 wt% and N 4.72 wt%; calc. for **1**: C 24.42 wt%, H 3.42 wt% and N 4.75 wt%. anal. for **2**: C 26.74 wt%, H 3.83 wt% and N 4.52 wt%; calc. for **2**: C 27.20 wt%, H 3.91 wt% and N 4.53 wt%. anal. for **3**: C 23.51 wt%, H 2.55 wt% and N 5.47 wt%; calc. for **3**: C 23.25 wt%, H 2.63 wt% and N 5.42 wt%. anal. for **4**: C 14.28 wt%, H 2.13 wt% and N 3.36 wt%; calc. for **4**: C 14.61 wt%, H 2.21 wt% and N 3.41 wt%.).

Structural description

Compound 1: Compound **1** crystallizes in the monoclinic space group *P*2$_1$/*n* (no. 14). There are two beryllium atoms and four phosphorus atoms in the asymmetric unit. Each beryllium atom is tetrahedrally coordinated by four oxygen atoms with the Be–O bond lengths in the region of 1.589(7)-1.627(7) Å. The phosphorus atoms are also tetrahedrally coordinated by oxygen atoms with the P–O bond lengths varying from 1.472(4) Å to 1.588(5) Å. Each BeO_4 tetrahedra shares four oxygen corners with adjacent PO_4 tetrahedra, but each phosphorus atom only makes two P–O–Be linkages to adjacent beryllium atoms. Such connectivity creates a unique three-dimensional open-framework structure. The negatively charged framework is balanced by the presence of MV dications within the pores, which occupy 48.7% of the unit cell volume (calculated using the program *PLATON*).[13]

Table 1. Crystal data and structure refinement for compounds **1**-**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{12}H_{20}Be_2N_2O_{16}P_4$	$C_{14}H_{24}Be_2N_2O_{16}P_4$	$C_{20}H_{27}Be_5N_4O_{28}P_7$	$C_5H_9Be_3NO_{13}P_3$
Formula weight	590.20	618.25	1033.30	411.07
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	Cc	P-1
a, Å	15.3327(4)	22.8218(3)	14.6958(4)	4.8173(3)
b, Å	9.5934(2)	21.6546(3)	11.6451(4)	12.0871(7)
c, Å	15.4363(4)	9.4920(1)	20.5912(6)	12.6085(9)
α, ^{o}	90	90	90	62.332(7)
β, ^{o}	97.199	91.300(1)	93.811(2)	79.518(5)
γ, ^{o}	90	90	90	84.052(5)
Volume, Å^3	2252.67(10)	4668.05(10)	3516.06(19)	639.21(7)
Z	4	4	4	2
D_c, g/cm^3	1.740	1.759	1.952	2.136
μ (Mo-Kα), mm^{-1}	3.881	3.777	0.469	5.091
Total data	20499	12573	7542	8994
Unique data	4027	4172	4955	2277
Data, I > 2σ(I)	3865	3716	4513	2045
Final R_1, wR_2 [I > 2σ (I)]	0.0888, 0.2500	0.0631, 0.1747	0.0415, 0.0926	0.0765, 0.2028

Compound **1** displays large 12 MR channels along the [100] and [001] directions. Viewed along the [010] direction, it possesses 8-ring and 16-ring channels (Fig. 1a). The diameters of the two different 12-ring windows and 16-ring window are about 6.1 Å × 8.0 Å, 7.1 Å × 7.6 Å, and 8.5 Å × 9.0 Å, respectively, calculated from the distance between the oxygen atoms across the windows. The framework density (FD) defined as the number of tetrahedra per 1000 Å^3 is 10.7 for compound **1**, which is lower than those of other crystalline beryllium phosphates. For example, the FD value is 11.7 for BePO-X, 14.1 for BET-P, 17.1 for BePO4-GME, 19.1 for BePO4-GIS, and 21.5 for BePO4-ABW.[5]

By regarding beryllium atoms as the 4-connected nodes and P-centered tetrahedra as the linkers, the framework structure of **1** can be understood as a zeolitic CrB_4 network (Fig. 1b).[14] As far as we know, such zeolitic topology has been observed for the first time in beryllium phosphate chemistry. It is well known that CrB_4-type zeolites only contain 8-ring channels. Notable examples include $K_{1.14}Mg_{0.57}Si_{1.43}O_4$, $K_{1.10}Zn_{0.55}Si_{1.45}O_4$, and $K_{1.11}Fe_{1.11}Si_{0.89}O_4$.[15] These compounds crystallize in the tetragonal space group $I4mm$ (no. 107) with a FD value of 18.9. The presence of 16-ring channels and a low framework density in the CrB_4-type structure of **1** is noteworthy.

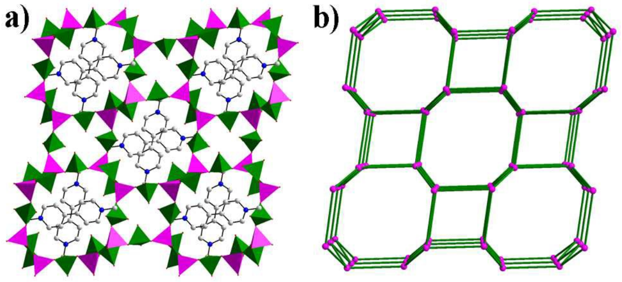


Fig.1. (a) A view of the structure of **1** along the [010] direction, showing the *in situ* generated MV dications within the 16 MR channels. (b) The compound has a zeolitic CrB_4 topology by regarding beryllium atoms as the 4-connected nodes and P-centered tetrahedra as the linkers. Color code: beryllium/BeO_4 tetrahedra, pink; HPO_4/H_2PO_4 tetrahedra, green; carbon, gray; nitrogen, blue; oxygen, red.

Compound 2: Compound **2** crystallizes in the monoclinic space group $C2/c$ (no. 15). The asymmetric unit contains 20 non-hydrogen atoms, of which two beryllium atoms and five phosphorus atoms are crystallographically independent. Each beryllium atom has a tetrahedrally coordinated geometry, bonded by four oxygen atoms with the Be–O bond lengths in the region of 1.610(4)-1.644(4) Å. Of the five independent phosphorus atoms, P(5) is disordered over two positions. Therefore, the occupancy for P(5) was assigned to be 0.5 in the refinement. The strict alternation of BeO_4 tetrahedra and PO_4 tetrahedra creates a three-dimensional structure with a low FD value of 10.3.

Compound **2** has the same framework topology as compound **1**, but different organic cations and pore apertures. Viewed along the [001] direction, the compound has two different types of 16 MR channels (Fig. 2). The circular window has the pore diameter of 8.9 Å × 9.7 Å, and the elliptical one has the pore diameter of

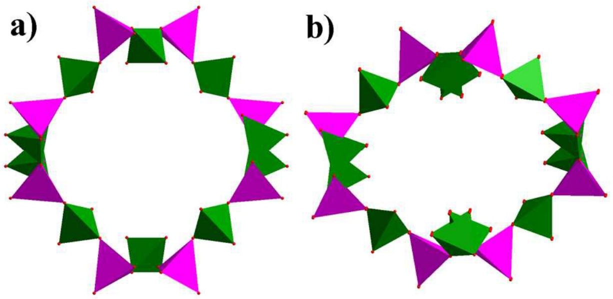


Fig.2. A view of the (a) circular and (b) elliptical 16 MR channels in compound **2** along the [001] direction.

7.4 Å × 9.1 Å. Intersecting these channels are two types of 12 MR channels with circular apertures, which run along the [110] and [1-10] directions, respectively. The EV cations are ordered within the channels, which occupy 50.3% of the unit cell volume.

It has been demonstrated that the use of large clusters as the building units in a zeolitic topology is favorable for the formation of large pore apertures. For example, the replacement of TO_4 tetrahedra in CrB_4-type zeolite by T2 clusters, the pore size will be enlarged from 8 MR to 16 MR (Fig. 3).[16] If the 4-connected nodes in the CrB_4 network are partial substituted by oxo boron clusters (i.e., B_4O_9 and B_5O_{10} units), open-framework structures with 12-ring channels are generated.[17] Another approach to enlarge the pore size of a specific zeolitic network as found in **1** and **2** reported here, is to insert 2-connected TO_4 tetrahedra between two adjacent 4-connected nodes in the network. This synthetic strategy may be useful for the preparation of other zeolitic structures with extra-large pores. For example, if 2-connected TO_4 tetrahedra were inserted into the FAU topology, the largest pore size may increase from 12 MR to 24 MR.

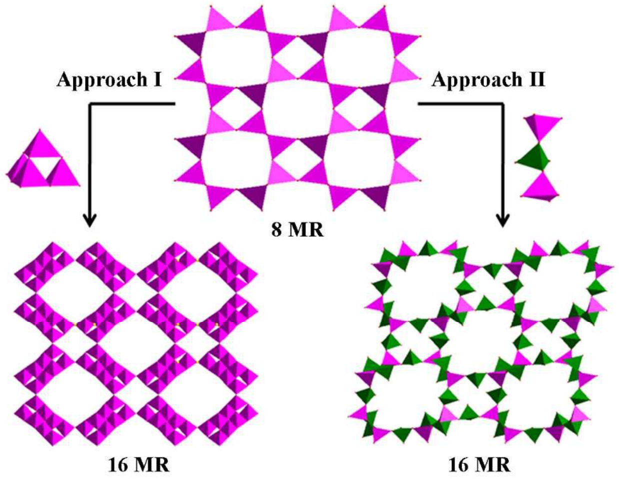


Fig.3. Two approaches to obtain CrB_4-type structures with 16 MR pores: Approach I is the use of T2 supertetrahedra as the building units, and Approach II is to insert 2-connected tetrahedra between adjacent 4-connected nodes.

Compound 3: Compound **3** crystallizes in the monoclinic space group *Cc* (no. 9). The asymmetric unit contains five beryllium atoms, seven HPO_4 groups, and two 4,4'-H_2bpy cations. The beryllium atoms are all tetrahedrally coordinated by oxygen atoms with Be–O bond lengths varying from 1.581(7) to 1.680(7) Å. Of the seven independent phosphorus atoms, P(1) atom makes two P–O–Be linkages to adjacent beryllium atoms, and the remaining phosphorus atoms each make three P–O–Be linkages to adjacent beryllium atoms. The P–O bond lengths are in the region of 1.462(4)-1.591(4) Å. Bond valence sum values indicate that P(1)–O(3), P(2)–O(8), P(3)–O(12), P(4)–O(15), P(5)–O(19), P(6)–O(22) and P(7)–O(27) with distances of 1.532(5), 1.556(4), 1.559(4), 1.591(4), 1.591(4), 1.562(4) and 1.560(3) Å are P–OH units.[18]

The strictly alternation of BeO_4 and HPO_4 tetrahedra forms a three-dimensional open-framework structure. Viewed along the [110] directions, compound **3** has two types of 12 MR channels (Fig. 4a). The atom-to-atom dimensions of the 12 MR windows are about 4.3 Å × 7.5 Å, and 7.3 Å × 8.7 Å, respectively. Similar 12 MR channels are also observed along the [1-10] direction. An interesting structural feature of **3** is the presence of large $4^{10}8^{4}12^{4}$ cages, as shown in Fig. 4b. Two diprotonated 4,4'-bpy cations are accommodated within the cage. These organic cations balance the negatively charged framework and occupy 46.3% of the unit cell volume.

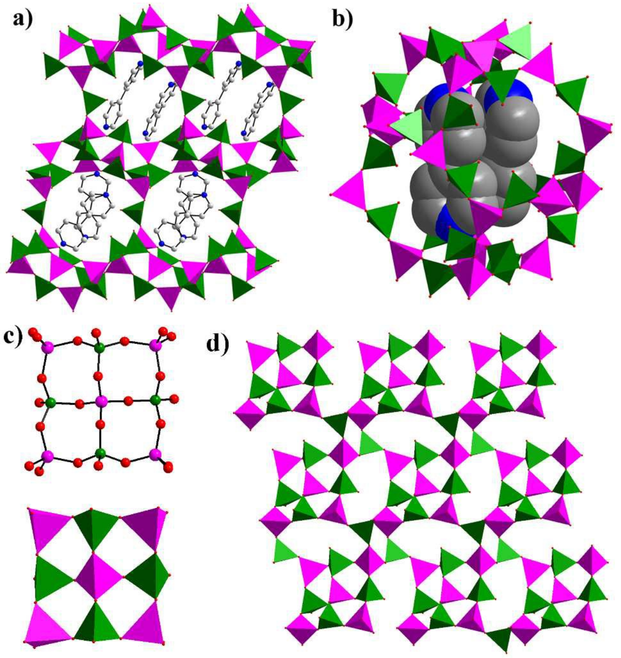


Fig.4. (a) A view of the framework structure of **3** along the [110] direction. (b) Polyhedral and space-filling representation of the $4^{10}8^{4}12^{4}$ cage encapsulating two 4,4'-H_2bpy cations. (c) Ball-and-stick and polyhedral representation of the 4-ring square. (d) A (3,4)-connected sheet containing the 4-ring square as the building block.

The framework structure of **3** is reminiscent of a chiral open-framework zinc phosphate ($NaZnPO_4 \cdot H_2O$) because both of them contain a square of 4-rings as their building block (Fig. 4c).[19] The unusual building block contains four HPO_4 tetrahedra and five BeO_4 tetrahedra. It can be conceptually built up by the following procedure. First, the alternation of four HPO_4 tetrahedra and four BeO_4 tetrahedra forms an 8 MR window. Then, the fifth BeO_4 tetrahedron is encapsulated in the center of the 8 MR by sharing oxygen vertices with the four HPO_4 tetrahedra to give rise to the square of 4-rings. Such building blocks are joined by 4 MRs into infinite sheets parallel to the *ab* plane (Fig. 4d), which are further pillared by $HP(1)O_4$ tetrahedra to produce the open-framework structure of **3**.

Compound 4: Compound **4** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit of **4** contains 25 non-hydrogen atoms, of which 19 atoms belong to the host framework and the remaining six atoms belong to the guest species. All the beryllium atoms and phosphorus atoms are tetrahedrally coordinated by oxygen atoms with the Be–O bond lengths in the region of 1.574(6)-1.702(6) Å and the P–O bond lengths in the region of 1.496(3)-1.572(3) Å. It is noteworthy that Be(3) atom only shares three oxygen vertices with adjacent phosphorus atoms, leaving one vertex occupied by OH group.

The linkages between BeO_4 tetrahedra and PO_4 tetrahedra create a three-dimensional structure. It displays one-dimensional 12 MR channels running along the [100] direction, as shown in Figure 5a. The diameter of the 12 MR is about 8.0 Å × 10.3 Å, calculated from the distance between two oxygen atoms across the window. The 2,2'-H_2bpy cations are ordered within the 12 MR channels, which occupy 31.9% of the unit cell volume.

Compound **4** has the same framework topology as the berylloarsenate BAF1011 and two open-framework beryllium phosphates, which contain monoprotonated pyridine or imidazole cations as the SDAs.[20] We demonstrate here that it is possible to synthesize this framework structure by using bulky 2,2'-bpy as the SDA. It is noteworthy that 2,2'-bpy display a different structure-directing role from that of 4,4'-bpy, although they have the similar size and shape. The different positions of the nitrogen atoms in the two SDAs induce different host-guest hydrogen-bonding interactions, which are sufficient to generate two different framework topologies.

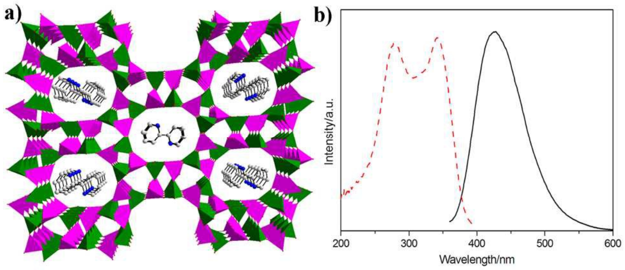


Fig.5. (a) A view of the structure of **4** along the [100] direction. (b) Excitation (red) and emission (black) spectra of **4** at room temperature.

TGA, fluorescent spectrum, and SHG measurement

Thermogravimetric analysis, carried out in a flow of air with a heating rate of 10 °C/min, showed that compounds **1-4** remained stable up to 250 °C, 280 °C, 350 °C, and 320 °C, respectively. (Fig. S5†). Although compounds **1** and **2** contain viologen cations within their intersecting channels, they didn't exhibit obvious photochromic behaviours when the two compounds were exposed to X-ray irradiation for several minutes. Upon excitation at 340 nm, compound **4** displayed a strong luminescence with a peak maximum at 428 nm (Fig. 5b). For compounds **1-3**, no fluorescent responses were observed in the measured region under the experimental conditions. The second harmonic generation (SHG) measurement for compound **3** was carried out on its powder sample at room temperature. The intensity of the green light (frequency-doubled output: 532 nm) produced by the sample exhibits a SHG efficiency about 0.1 times that of KDP (KH_2PO_4) powder, confirming the absence of a center of symmetry for this compound (Fig. S6†).

Conclusions

In summary, two open-framework beryllium phosphates with a zeolitic CrB_4 topology were synthesized under solvothermal conditions. The two compounds contain *in situ* generated viologen cations within their intersecting 12 MR, 12 MR and 16 MR channels. Comparative studies shows that the pore apertures of their structural analogues templated by 4,4'-H_2bpy or 2,2'-H_2bpy cations are delimited by 12 tetrahedra, demonstrating the great potential of bulky viologen ions as SDAs for the construction of new zeotype structures with extra-large channels.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray data, additional figures, IR spectra, powder XRD patterns, TGA curves. See DOI: 10.1039/b000000x/

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Two 16-membered-ring beryllium phosphates with a zeolitic CrB_4 topology have been prepared under solvothermal conditions, which contain *in-situ* generated viologen ions from the alkylation of 4,4'-bipyridine molecules.