# Chemical Science

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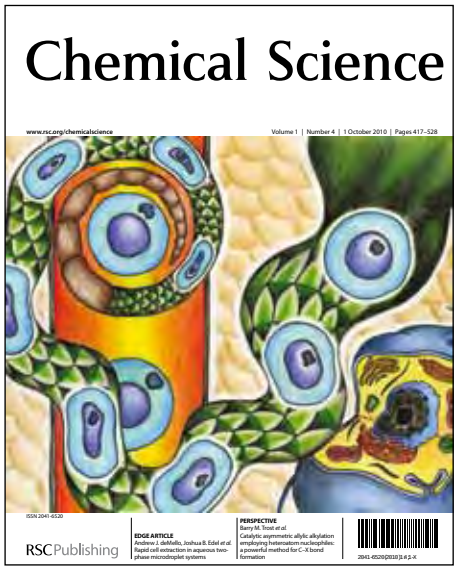


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ARTICLE

# Organic-Inorganic Hybrid Polyhedra That Can Serve as Supermolecular Building Blocks

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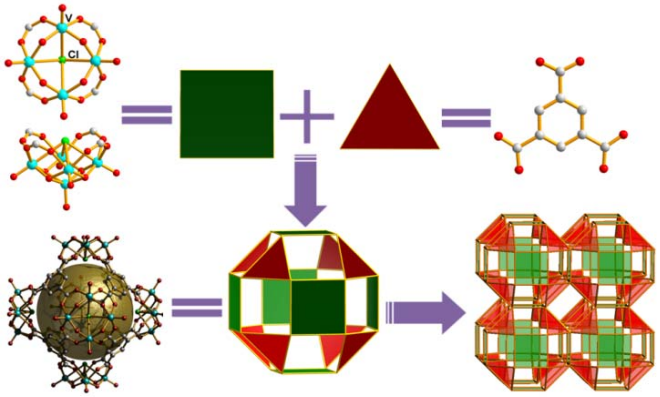
$[V_4O_8X(COO)_4]^{z-}$ or $[V_5O_9X(COO)_4]^{2-}$ polyoxometallate anions can function as 4-connected nodes that assemble with 3-connected organic nodes (1,3,5-benzentricarboxylate) to afford *small cubicuboctahedral* hybrid nanoballs (**hyball-3**, **-4**, **-5**) in high yield. The resulting polyhedral cages exhibit 550 Å$^3$ internal volumes and gas sorption measurements reveal that solid forms of the **hyballs** are permanently porous. The exterior surfaces of the **hyballs** are suited for further self-assembly and **hyball-3** can serve as an octahedral supermolecular building block for the generation of primitive cubic (**pcu**) nets *via* two types of linkage: hydrogen bonds or coordination bonds.

## Introduction

The modular nature of metal-organic materials (MOMs) that results in their structural and functional diversity means that MOMs have attracted intense research activity over the past two decades.[1] MOMs that are sustained by nanoscale polyhedral building blocks (nanoballs) that in effect serve as supermolecular building blocks, SBBs, are an important subset of MOMs and they include extra-large surface area materials with surface areas up to 10,000 m$^2$/g.[2] Such MOMs enable studies that take advantage of porosity in the context of gas sorption,[3] drug delivery[4] and catalysis.[5] Such MOMs take advantage of the symmetry and exterior functionality of nanoballs by exploiting them as SBBs that are cross-linked by organic ligands or metal moieties.[6] For example, the prototypal nanoball is based upon square paddlewheel moieties that are linked at their vertices by 1,3-benzenedicarboxylate anions to form a discrete *small rhombihexahedron.*[7] This nanoball has been exploited as an SBB to form **tbo**,[8] **rht**[9] and **pcu**[10] nets. MOMs that are based upon polyhedral nanoballs are most typically synthesized via one-pot processes.[11] However, Zhou *et al.*[12] and Su *et al.*[13] recently reported isolation of nanoballs before cross-linking with 4,4'-bipyridine to form **pcu** and **fcu** nets, respectively.

Polyoxometalates (POMs) are exemplified by soluble anionic high oxidation state metal oxide clusters of d-block transition metals (especially $W^{VI}$, $Mo^{V,VI}$ and $V^{IV,V}$) and have also attracted considerable attention for their structure and properties.[14] In the context of MOMs, POMs have been used as nodes to generate polyoxometalate metal-organic frameworks (POMOFs)[15] or encapsulated as guests (POM@MOFs).[16] However, although POM nanoballs based upon regular polyhedra have been reported, they are purely inorganic as they are sustained by O-M-O bonds.[17] Organic-inorganic hybrid nanoballs (**hyballs**) in which POMs serve as molecular building blocks (MBBs) that are linked by organic ligands to form polyhedra remain underexplored. Indeed, we are aware of only two examples: Schmitt's POM capsule (**hyball-1**) formed from a POM and organoarsonic or phosphonic acids;[18a,b] Yang's cube from $Ni_6$-POMs linked by 1,3,5-benzenetricarboxylate (BTC) (**hyball-2**).[18c]

In this contribution, we introduce a third class of **hyball** based upon well-known[19,20] POMs with carboxylate ligands at their periphery. These shuttlecock-like vanadium POMs, V-POMs, $[V_4O_8X(COO)_4]^{z-}$ (X = $Cl^-$, $Br^-$, $NO_3^-$ and $K^+$; z = 1 or 2) and $[V_5O_9X(COO)_4]^{2-}$, are suited to sustain *cubicuboctahedral* nanoballs since V-POMs and BTC can serve as square and triangular faces, respectively (Scheme 1). They therefore follow one of the three design principles that have been successfully applied to nanoballs: vertex-directed;[21] face-directed (molecular paneling);[22,23] edge directed[22] self-assembly. These approaches afford polyhedra with windows and faces, faces only or windows only, respectively. Herein we address the use of V-POMs as square MBBs that are vertex-linked by 3-connected 1,3,5-benzenetricarboxylate, BTC, anions. The resulting *small cubicuboctahedral* hyballs (**hyball-3**, **-4**, **-5**) can in turn serve as SBBs for the generation augmented **pcu** nets (Scheme 1).




**Scheme 1. Hyball-3, -4** and **-5** are comprised of eight triangular faces (3-connected BTC anions) and six square faces (4-connected V-POMs) that are vertex-linked so as to form a *small cubicuboctahedron*; **Hyball-3** can serve as a 6-connected octahedral SBB to afford augmented **pcu** nets *via* coordination bonding or hydrogen bonding at its square faces.

## Results and discussion

Reaction of $H_3BTC$ with $VCl_3$ in N,N-dimethylacetamide (DMA) and $H_2O$ affords dark green rhombic crystals of **hyball-3**: $(NH_2Me_2)_6[(V_4O_8Cl)_6(BTC)_8]\cdot$[Solvent] (Solvent = DMA, $H_2O$). Single crystal x-ray diffraction (SCXRD) revealed that **hyball-3** adopts the tetragonal space group *I4/m* with $a = b = 21.1256(6)$ Å and $c = 27.4118(14)$ Å. **Hyball-3** is comprised of six tetranuclear $[V_4O_8Cl(COO)_4]^{1-}$ MBBs linked by eight triangular BTC ligands (Fig. 1a). Each vanadium cation exhibits octahedral geometry through two $\mu_2$-$\eta^1\eta^1$ carboxylate moieties, two $\mu_2$-$O^{2-}$ ligands, one terminal $O^{2-}$ ligand and one $\mu_4$-$Cl^-$ ligand. The -6 charge of each **Hyball-3** anion is balanced by six $[NH_2Me_2]^+$ cations (there are six monoanionic $[V_4O_8Cl(COO)_4]^-$ MBBs per **hyball-3**). Fig. S1 reveals that V1, V2, V3 and V4 are assigned to be $V^V$ with V=O bond distances ranging from 1.591(4) to 1.602(4) Å and V-O bond distances from 1.794(3) to 2.042(3) Å.[24] The $\mu_4$-$Cl^-$ moiety caps a square pyramid with V-Cl bonds of 2.795(5) to 2.852(1) Å. Bond valence sum (BVS) calculations[25] (Table S1) support $V^V$, as does a previous report.[20] **Hyball-3** has an outer diameter of ~20 Å, and an inner diameter of ~14 Å. The estimated internal volume of **hyball-3** is ~550 $Å^3$ but its windows are too small to allow ingress and egress (1.0 Å × 2.3 Å after subtracting *van der Waals* radii). Each **hyball** is connected to four adjacent hyballs by two $[NH_2Me_2]^+$ cations to form an H-bonded 2D square grid net *via* charge assisted O···H-N-H···O hydrogen bonds (Fig. 2 left and Fig. S2). The 2D H-bonded layers stacking in ABAB fashion along the *c* direction. The A-A distance between square grid layers is 11.8 Å (the nearest V···V distance). There are free $[NH_2Me_2]^+$ cations and solvent molecules located within the H-bonded layers to balance the extra charge for each hyball and fill the pore spaces. Crystals of **hyball-3** were observed to undergo a phase change to a new crystalline phase, **hyball-3′**, when exposed to the atmosphere for 2 weeks. SCXRD revealed that **hyball-3′** adopts the tetragonal space group *P4/n* with $a = b = 21.049(1)$ Å and $c = 21.633(4)$ Å. As shown in Fig. S2 and S3, an overall comparison of the **hyball** packing in **hyball-3′** and **hyball-3** revealed that there were only slight differences between the two structures in the *ab* plane as **hyball-3′** forms a H-bonded square grids similar to those observed in the *ab* plane of **hyball-3** (Fig. S3). However, the hyballs pack much closer along the *c* direction with the distance between square grid layers shrinking from 11.8 to 6.1 Å in **hyball-3′** because of a rearrangement of $[NH_2Me_2]^+$ cations in the pores. This rearrangement means that A-layers are now cross-linked along the *c* direction by V-O···H-N-H···O-V hydrogen bonds from $[NH_2Me_2]^+$ cations. The resulting architecture can be described as an H-bonded **pcu** net (Fig. 2, right). B-layers are likewise cross-linked to produce a doubly interpenetrated **pcu** network.

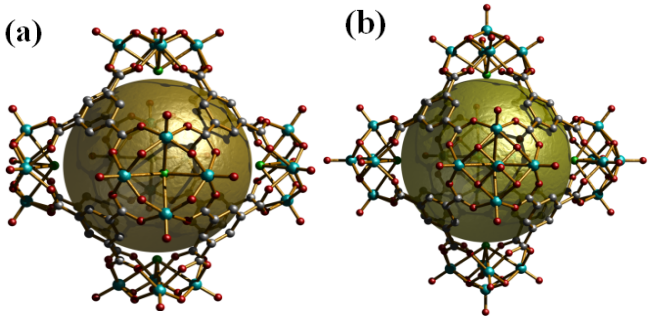



**Fig. 1.** The structures of (a) **hyball-3** and (b) **hyball-4**.

The same conditions used to prepare **hyball-3** but with N,N-dibutylformamide (DBF)/$H_2O$ as solvent afforded **hyball-4**, $(NH_2(Butyl)_2)_{12}[(V_5O_9Cl)_6(BTC)_8]\cdot$[Solvent]. SCXRD revealed that **hyball-4** crystallizes in the rhombohedral space group *R*-3*c* with $a = b = 34.773(3)$ Å and $c = 39.676(3)$ Å. **Hyball-4** consists of 6 pentanuclear $[V_5O_9Cl(COO)_4]^{2-}$ clusters linked by 8 BTC ligands (Fig. 1b). A $V^v$ cation is located above four basal $V^{IV}$ cations (Fig. S4). The oxidation states for the vanadium cations are consistent with previous reports[20a,26] and further supported by BSV calculations as detailed in Table S2. The apical $V^v$ atom is five-coordinate and adopts square pyramidal geometry through four $\mu_2$-$O^{2-}$ and one terminal $O^{2-}$ anion. V=O bond distances range from 1.572(9) to 1.594(9) Å while V-O bond distances range from 1.836(9) to 2.036 (10) Å. The existence of hyballs with either tetranuclear $[V_4O_8X(COO)_4]^{z-}$ or pentanuclear $[V_5O_9Cl(COO)_4]^{2-}$ MBBs prompted us to explore whether mixed MBBs might also result in hyballs. This was indeed accomplished by increasing the proportion of $VCl_3$ used in the synthesis of **hyball-3**, thereby affording dark green rhombic crystals of **hyball-5** of a formula $(NH_2Me_2)_8[(V_4O_8Cl)_{3.8}(V_5O_9Cl)_{2.2}(BTC)_8]\cdot$[Solvent]. The formula was determined by refinement of the site occupancy factor of the $V^v$ moiety. In **hyball-5** the ratio of tetranuclear $[V_4O_8X(COO)_4]^{z-}$ to pentanuclear $[V_5O_9Cl(COO)_4]^{2-}$ MBBs is ca. 3.8/2.2. **Hyball-5** (*I4/m*, $a = b = 21.1683(5)$ Å and $c = 27.3991(15)$ Å) is isostructural with **hyball-3**.

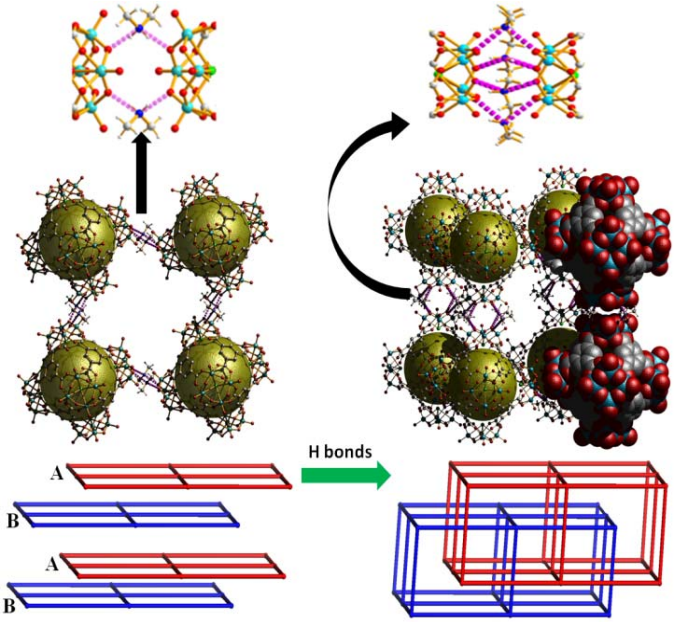



**Fig. 2.** The H-bonded 2D square grid net (left, viewed looking at the *ab* plane) of **Hyball-3** converts to **Hyball-3′**, a doubly interpenetrated **pcu** net, upon exposure to air for 2 weeks (right).

**Hyball-3**, **-4** and **-5** were activated for gas sorption studies by exchanging with MeOH for three days and then heating at 60 °C for 10 h under vacuum. The powder X-ray diffraction patterns (PXRDs) of **hyball-3** and **-5** measured after activation were found to closely match those of **hyball-3′** indicating that removal of guest solvent molecules promote the phase change **hyball-3** to **hyball-3**. All three materials were found to be permanently porous following activation. Gas sorption studies revealed that **hyball-3**, **-4** and **-5** adsorb $CO_2$ with uptakes of 82.0, 56.5 and 60.7 $cm^3/g$ respectively at 195K and $P/P_0 = 0.95$, corresponding to Langmuir surface areas (calculated from the pressure region 10-100 mmHg) of 313.2, 56.0 and 199.4 $m^2/g$, respectively (Fig. 3a). Fig. 3b presents the $CO_2$ gravimetric uptake at 298 K and 1 atm, which were observed to be 27.0, 9.1 and 22.6 $cm^3/g$ for **hyball-3**, **-4** and **-5** respectively. As shown in Fig. S5, **hyball-3** and **-5** exhibit type I $N_2$ sorption isotherms with uptakes of 74.0 and 61.4 $cm^3/g$ at 77K and $P/P_0$=0.95 whereas **hyball-4** was found to be non-porous with respect to $N_2$. The observed porosity

can be ascribed to be the interstitial spaces between adjacent hyballs since the windows (~1.0 Å × 2.3 Å) of the hyballs are too small to allow passage of $N_2$ or $CO_2$.[27] The isosteric heat of adsorption ($Q_{st}$) for $CO_2$ was calculated using the virial method from $CO_2$ isotherms collected at 273 and 298 K (Fig. S6). **Hyball-3**, **-4** and **-5** exhibit $Q_{st}$ for $CO_2$ of 28.8, 24.4 and 33.2 kJ/mol, respectively, at zero coverage. IAST calculations[28] based on the experimental $CO_2$ and $CH_4$ isotherms at 298K suggest initial $CO_2/CH_4$ selectivities of 7.7, 2.0 and 7.6 for **hyball-3**, **-4** and **-5**, respectively (Fig. S7).

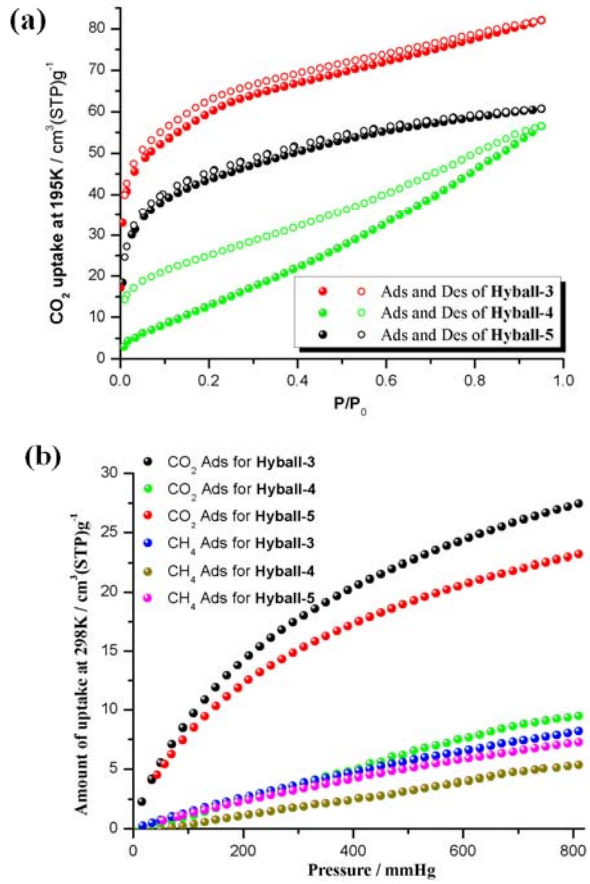



**Fig. 3.** Gas adsorption isotherms for **hyball-3**, **-4** and **-5**: (a) $CO_2$ at 195K; (b) $CO_2$ at 298K and $CH_4$ at 298K.

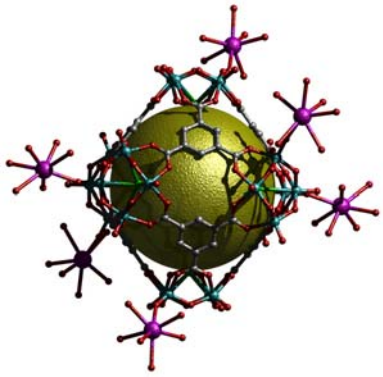


**Fig. 4.** Each hyball is cross-linked by six $Ba^{2+}$ cations in **hyball-3-Ba**.

The peripheral portions of the polyoxovanadate clusters in **hyball-3** are rich in oxygen atoms that are oriented in such a manner that a concave surface exists for each MBB. This surface seems well-suited to coordinate with metal cations. Further, **hyball-3** is anionic and soluble in polar solvents like $H_2O$, dimethylformide (DMF), DMA and dimethyl sulfoxide (DMSO). We therefore explored if **hyball-3** can indeed serve as an SBB in network structures when a 2-step synthetic strategy[12,13] is applied. Dissolution of **hyball-3** in DMA/$H_2O$ resulted in a dark green solution and layering of this solution with $BaCl_2$ in MeOH for one week afforded hexagonal green crystals of $(Ba(Solvent)_8)_2[(V_4O_8Cl)_6(BTC)_8Ba_3(Solvent)_{15}]\cdot$[Solvent], **hyball-3-Ba**. **Hyball-3-Ba** crystallizes in the monoclinic *C2/c* space group with a unit cell of $a$ = 37.3416(11) Å, $b$ = 21.5080(6) Å, $c$ = 36.8796(10) Å, $\alpha = \gamma = 90°$ and $\beta$ = 109.771(1)°. Conversely, a one-pot reaction of $VCl_3$, $H_3BTC$ and $BaCl_2$ produced a yellowish-green solution but no crystals. A SCXRD study was conducted upon **hyball-3-Ba** and revealed that it is an augmented **pcu** (**pcu-a**) network in which each **hyball** serves as a 6-connected octahedral SBB linked by V=O-Ba-O=V bridges (Fig. 4). The resulting polyhedron based net is as depicted in Scheme 1. Fig. 5 reveals that hyballs are connected by seven-coordinated $Ba^{2+}$ ions to produce a square grid net along the *bc* plane. These square grid nets are further cross-linked by bridging $Ba^{2+}$ ions along the *a* direction to form an augmented **pcu** net. $[Ba(solvent)_8]^{2+}$ cations lie in the channels to balance the negatively charged $[(V_4O_8Cl)_6(BTC)_8Ba_3(Solvent)_{12}]^{4-}$ framework. V=O bond distances range from 1.570(8) to 1.596(5) Å and V-O bond distances range from 1.830(9) to 2.038 (10) Å. Ba-O bonds exhibit an average distance of 2.901(2) Å, which is within expected values.[29] **Hyball-3-Ba** was activated for gas adsorption using a similar procedure to that used for **hyball-3** and $N_2$ and $CO_2$ were tested to evaluate its porosity. At 77K and $P/P_0$ = 0.95, **Hyball-3-Ba** exhibits $N_2$ uptake (Fig. S8) of 35.8 $cm^3/g$ that corresponds to a Langmuir surface area of 113.8 $m^2/g$. $CO_2$ gravimetric uptake for **Hyball-3-Ba** was observed to be 26.0 $cm^3/g$ at 298 K and 1 atm (Fig. S9).

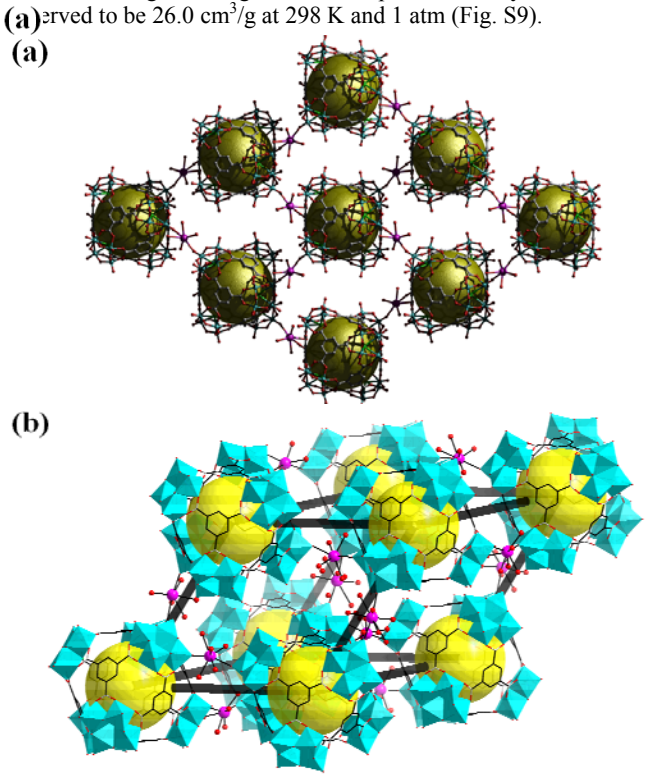



**Fig. 5.** (a) Hyballs in **hyball-3-Ba** are connected by $Ba^{2+}$ ions to form a square grid net along the *bc* plane; (b) these square grid nets are further linked by $Ba^{2+}$ cations to produce a **pcu** network (highlighted by black lines, Ba pink, V, turquoise).

## Conclusions

In conclusion, we have demonstrated that BTC self-assembles with tetranuclear and pentanuclear V-POMs to form a new family of hybrid nanoball structures (**hyballs**), **Hyball-3**, **-4**, **-5**. These **hyballs** are robust, permanently porous and their exterior surfaces facilitate cross-linking to generate **pcu** nets. Such materials are likely to exhibit promise as catalysts or biosensors and are being further investigated in our laboratory in this context.

## Acknowledgements

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## Notes and references

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†Electronic supplementary information (ESI) available: experimental sections, PXRD, TGA, gas sorption, $CO_2/CH_4$ selectivity, crystal supporting figures, tables of BVS calculation, and CCDC 965262 to 965266. For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/xOxxOOOOOx.

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