JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis

Michael T. Wharmby,[†] John P. S. Mowat,[†] Stephen P. Thompson,[‡] and Paul A. Wright*,[†]

[†]School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews, Fife KY16 9ST, United Kingdom
[‡]Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom

Supporting Information

ABSTRACT: Crystalline microporous cobalt and nickel bisphosphonates with a hexagonal array of one-dimensional channels 1.8 nm in diameter have been prepared hydrothermally and provide the first example of the use of isoreticular chemistry in the synthesis of phosphonate metal−organic frameworks. The materials contain both physisorbed and coordinating water molecules in the as-prepared form, but these can be removed to give permanent extra-large microporosity, with pore volumes of up to 0.68 $cm^3\ g^{-1}$, and coordinatively unsaturated sites, with concentrations up to 4.25 mmol g^{-1}.

The preparation of crystalline microporous solids with pore openings greater than 1 nm has long been an important target for those interested in the adsorption, separation, and catalytic conversion of large organic molecules. Aluminosilicate zeolites with such large pores, which could be used in the catalytic refining of the heavy fraction of crude oil, have not yet been prepared, but extra-large pore germanosilicates with pores openings up to 1.2 nm, such as ITQ-33[1] and ITQ-44,[2] are exciting recent developments in this field. The synthesis of metal−organic frameworks (MOFs) with pore openings larger than 1 nm does not suffer from the same restrictions imposed by the tetrahedral building units of zeolites. The use of rigid linkers, such as 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic (trimesic) acid, 2,6-naphthalenedicarboxylic acid, and 1,3,5-benzenetribenzoic acid, has permitted the preparation of structures with pore openings above 1 nm and cages well into the mesoporous regime (>2 nm). The metal carboxylates MIL-101(Cr)[3] and MIL-101_NDC(Cr),[4] MOF-177(Zn),[5] MesoMOF-1(Tb),[6] and UMCM-1(Zn)[7] provide examples of such structures, with three-dimensional connectivity through windows with free diameters of 1−2 nm. One approach toward the designed preparation of extra-large-pore MOFs, jointly termed *scale chemistry*[8] and *isoreticular chemistry*,[9] is through the use of building units of increasing size and with the same coordination geometry. This yields solids with the same framework topology but with increased dimensions and consequently increased pore and pore window sizes. The IRMOF series of isoreticular zinc carboxylates built from linear dicarboxylates is one example,[10] and the MesoMOF-1[6] structure (with the same topology as the MIL-100[11] structure but with triazine-1,3,5-tribenzoate in place of the smaller trimesate) is another example of isoreticular MOF chemistry.

We have recently shown that it is possible to prepare large-pore metal phosphonate MOFs that possess coordinatively unsaturated sites when dehydrated. The STA-12 series (St Andrews microporous material number 12) of metal *N*,*N*′-piperazinebis(methylenephosphonate) materials (Figure 1), prepared with divalent Mn, Fe, Co, and Ni cations,[12−14] has a pore size of 0.9 nm when dehydrated and 5-fold coordinatively unsaturated metal sites, which are able to interact as Lewis acids. The aim of the present work was to prepare metal bisphosphonate MOFs with larger pore sizes via isoreticular synthesis, which had not previously been used in the crystallization of porous phosphonate MOFs. Such solids would be of interest in gas adsorption and separation, as catalysts or catalyst supports, and in drug delivery. Zirconium and aluminum phosphonates[15−17] with pore size distributions extending into the 1−2 nm domain have previously been prepared, but the porosity in these materials results from disorder within pillared layered structures and is not crystallographically well defined.

Examination of the topology of STA-12 indicated the structure would be capable of supporting an extended linker possessing a geometry similar to that of the *N*,*N*′-piperazinebis(methylenephosphonic acid) (H_4**L**) used in its preparation. 4,4′-Bipiperidine may be thought of as an elongated analogue of piperazine, and thus the modified Mannich reaction, previously reported for the syntheses of H_4**L** and its 2-methyl and 2,5-dimethyl derivatives,[18] was used to prepare the phosphonic acid *N*,*N*′-4,4′-bipiperidinebis(methylenephosphonic acid) (H_4**LL**). (Full details of synthesis and characterization of the ligand are given in the Supporting Information.) Crystallographic analysis of H_4**LL** suggested it as a likely candidate for isoreticular synthesis, being centrosymmetric about the C−C bridge linking the two rings, thus showing similarity to H_4**L**, which is centrosymmetric about the center of the piperazinyl ring. Such a configuration of the rings in H_4**LL** could enable the formation of an STA-12-like structure.

Initial hydrothermal syntheses were performed using cobalt(II) acetate tetrahydrate (Sigma) and H_4**LL**, using the ratio 2.0:1.0:2.0:1000 ($Co(AcO)_2$:H_4**LL**:KOH:H_2O), which was previously successful in preparing STA-12 using H_4**L**,[12] as a starting point and varying the metal-to-ligand ratio (M:L) from 0.5:1.0 to 2.5:1.0. The base plays a dual role, initially solubilizing the ligand and subsequently controlling the pH during reaction. After aging at room temperature for 30 min, reactions were heated at 220 °C for 72 h. Reactions with a M:L of close to 2.0:1.0 yielded a purple microcrystalline powder, later determined to be phase pure, with

Received: November 1, 2010
Published: January 7, 2011

dx.doi.org/10.1021/ja1097995 | *J. Am. Chem. Soc.* 2011, 133, 1266–1269

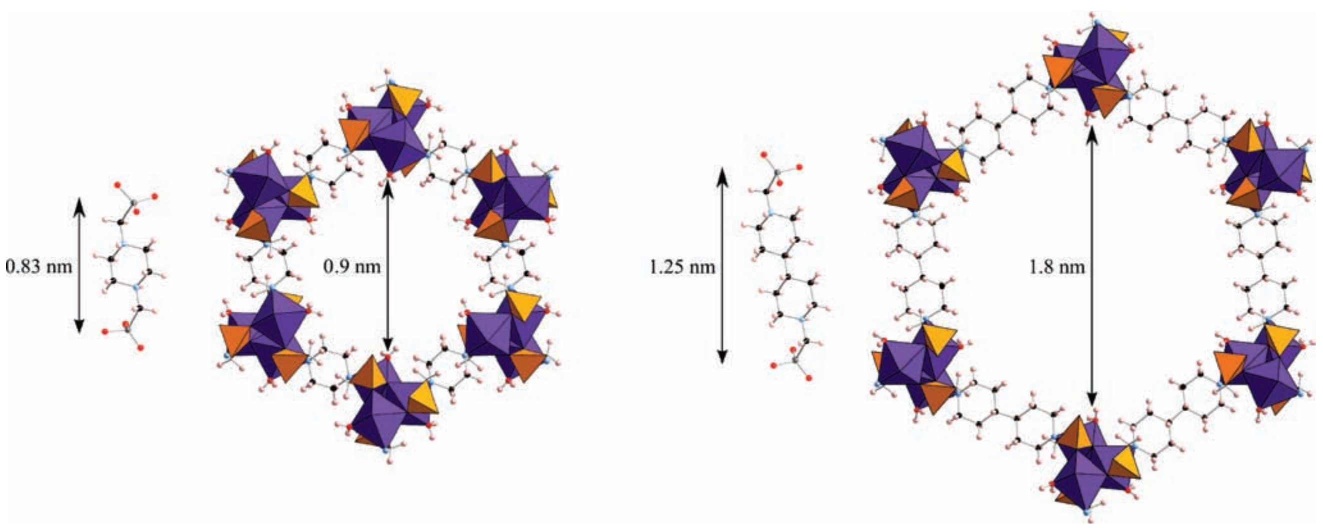

Figure 1. Comparison of the channel diameters and bisphosphonate linkers used in the preparation of the isoreticular framework materials STA-12[12−14] (left) and STA-16 (right).

a characteristic laboratory powder X-ray diffraction (PXRD) pattern (Supporting Information). This was indexed using DICVOL[19] and refined by Le Bail fitting in the GSAS suite of programs[20] to give a rhombohedral cell (hexagonal setting, a = 41.2874(6) Å, c = 6.2605(3) Å) and was designated STA-16(Co). Thermogravimetric analysis (TGA) of STA-16(Co) in air at 1.5 °C min^{-1} up to 900 °C (Supporting Information) shows a weight loss of 26.2 wt% (17−52 °C), assigned to the loss of physisorbed water, immediately followed by a second loss of 6.7 wt%, assigned to the loss of one coordinated water molecule per Co^{2+} (expected value, 5.2 wt%), which was complete by 120 °C. The discrepancy is attributed to loss of some residual physisorbed water in the second event. This water loss is followed by a plateau until 230 °C, after which thermal decomposition of the solid occurs. Energy-dispersive X-ray analysis indicated a Co:P of 1.0, and, in combination with the TGA results, a composition for STA-16(Co) of $Co_2(H_2O)_2$**LL**$\cdot 11H_2O$, where **LL** = $C_{12}H_{22}N_2P_2O_6$, was postulated, which was found to be in reasonable agreement with the synthesized material by elemental analysis (expected, C = 20.6%, H = 6.8%, N = 4.0%; observed, C = 22.0%, H = 6.9%, N = 4.3%).

The composition, water loss behavior, and particularly the similar symmetry and c parameter, but larger unit cell parameter in the a dimension, compared with the STA-12 structure [unit cells at room temperature: STA-16(Co), a = 41.2874(6) Å, c = 6.2605(3) Å; STA-12(Co),[14] $R\bar{3}$, a = 28.024(3) Å, c = 6.2734(8) Å] all suggested a model for STA-16(Co) consistent with the targeted isoreticular version of STA-12. A geometric model for STA-16 was therefore constructed, starting from the structure of STA-12(Ni),[13] replacing N,N'-piperazinebis(methylenephosphonate) (**L**) groups with N,N'-4,4′-bipiperidinebis(methylenephosphonate) (**LL**) units. The $R\bar{3}$ symmetry of the original solid can be retained, because both molecules can adopt the same local symmetry (with the inversion center in **L** being replaced by that in **LL**, midway along the C−C bond linking the two piperidine rings). The model of STA-16 was also assumed to retain the axial arrangement of the coordinating α-aminomethylphosphonate groups (NCH_2PO_3).

This model was subsequently used as a starting point for Rietveld refinement against synchrotron PXRD data collected on beamline I11[21] at the Diamond Light Source using the GSAS program suite.[20] Approximate starting positions were included for physisorbed water, estimated by comparison with the positions of water molecules in STA-12(Ni),[13] with additional positions derived by difference Fourier analysis. (Full details of the refinement are given in the Supporting Information.) The final profile fit is given in Figure 2, which shows very good agreement between the observed diffraction pattern and that simulated from the refined structure (shown in Figure 3). This indicates that STA-16(Co) is an isoreticular version of STA-12, in which the short **L** ligand is substituted by the longer ligand, **LL**.

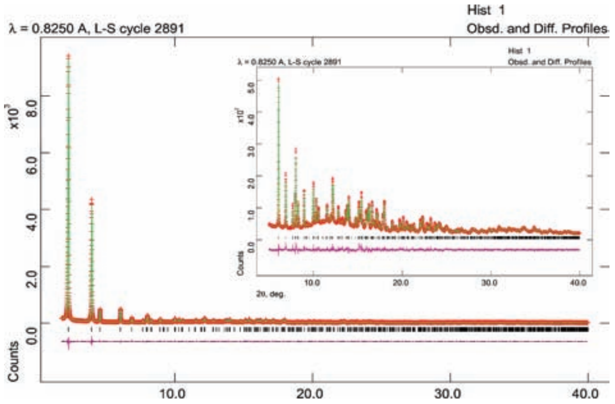

Figure 2. Rietveld plots of range 2−40° 2θ and 5−40° 2θ (inset) for the structure refinement of hydrated STA-16(Co) from synchrotron powder X-ray diffraction data, measured at 100 K, showing measured data (red), fitted data (green), and the difference plot (purple).

As in the STA-12 structure, the metal cations in STA-16 are coordinated in a distorted octahedral geometry by four phosphonate O atoms, one piperazinyl N atom, and the O atom of a water molecule (Co−O, 1.941(9)−2.240(14) Å; $Co-OH_2$, 2.042(9) Å; Co−N, 2.244(14) Å). These CoO_5N octahedra share edges to form metal phosphonate spirals. Each spiral is connected to three others to form a hexagonal array of channels parallel to the c-direction, with a free diameter of 1.8 nm. One P=O bond from each phosphonate group projects into the channels, where it H-bonds with physisorbed water (O1···O101, 2.819(15) Å), which also H-bonds to the water molecule

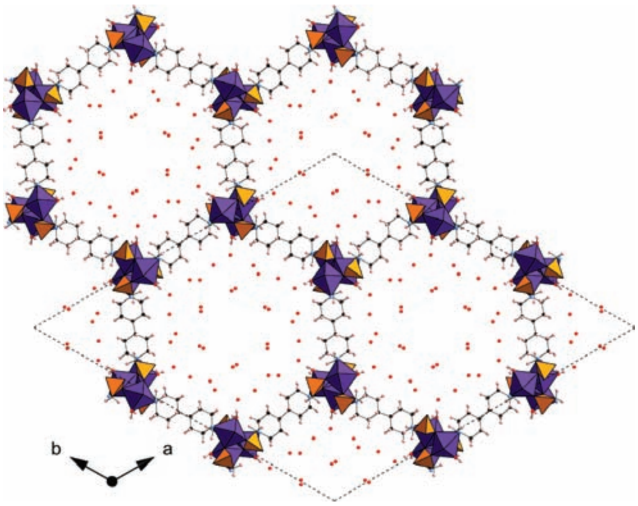

Figure 3. Refined structure of hydrated STA-16(Co), showing the hexagonal arrangement of channels and the position of the O atoms of physisorbed water molecules (in red) within the pores. Dashed lines indicate one unit cell.

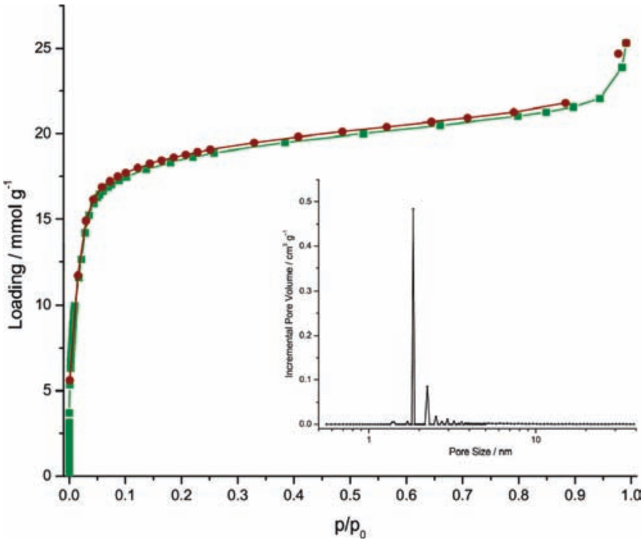

Figure 4. Adsorption and desorption isotherms of N_2 uptake on dehydrated STA-16(Co) at 77 K. Inset: Nonlinear DFT-calculated pore size distribution, assuming cylindrical pores.

coordinating the Co^{2+} cation. Other water molecule O atoms are located in the channels, with fractional occupancies in the range 0.40−0.79 and with reasonable H-bonding distances between them (for example, O106···O104, 2.86(3) Å). Overall, the refined composition was $Co_2(H_2O)_2$**LL**·$7.5H_2O$.

Physisorbed water molecules are fully removed by heating for 3 h in air or under vacuum at 150 °C (Supporting Information). Dehydration of the material, even under relatively mild conditions, results in a color change from purple to dark blue (Supporting Information), which indicates a change in the coordination environment of the Co^{2+}, thought to be due to the loss of the coordinated water molecule, in addition to the physisorbed water. The dehydrated structure is thought to have a coordinatively unsaturated site (CUS) density of 4.25 mmol g^{-1} (dry weight). Similar loss of physisorbed and coordinated water has previously been observed to occur in STA-12(Ni), to leave 5-fold-coordinated Ni^{2+}.[13] Synchrotron X-ray diffraction data (Supporting Information) indicates that crystallinity is retained upon dehydration of STA-16(Co) under vacuum, but that a complex distortion away from rhombohedral symmetry occurs. Dehydrated STA-12(Ni) also shows distortion, to triclinic symmetry, but a similar triclinic distortion does not provide a suitable model for the symmetry change in dehydrated STA-16(Co). The rhombohedral symmetry and purple color of STA-16(Co) return rapidly if the dehydrated solid is allowed to adsorb water from moist air, and crystallinity is fully restored (Supporting Information).

Nitrogen adsorption data measured volumetrically at 77 K on dehydrated STA-16(Co) using a Micromeritics ASAP 2020 porosimeter (Figure 4) indicate a pore volume of 0.68 cm^3 g^{-1} (at $p/p_0 = 0.4$). The inflection in the isotherm at $p/p_0 = 0.025$ is characteristic of pores approaching the mesopore regime: nonlinear DFT calculations for N_2 at 77 K, assuming a cylindrical pore with an oxide surface, indicate a pore diameter of 18.5 Å (Supporting Information).[22−24] This indicates that the distortion away from rhombohedral symmetry, observed by powder diffraction, affects the pore size only slightly (as also observed for STA-12(Ni)[13]), so that dehydrated STA-16(Co) has permanent porosity approaching the mesoporous regime.

Hydrothermal synthesis under similar conditions using nickel(II) acetate tetrahydrate (Sigma) rather than cobalt(II) acetate, but without base, gave a light green microcrystalline powder that was identified by PXRD as STA-16(Ni). Laboratory PXRD data for STA-16(Ni) were refined using the Le Bail fitting routines in GSAS,[20] with the cell of STA-16(Co) as a starting model, to give a similar rhombohedral cell with a = 41.052(7) Å and c = 6.1990(17) Å (hexagonal setting). TGA data indicate weight loss behavior similar to that of STA-16(Co), losing 22.4 wt% up to 48 °C, assigned to the loss of physisorbed water. Chemisorbed water is removed in a two-step process (complete by 148 °C) similar to that observed in STA-12(Ni).[13] STA-16(Ni) loses 4.4 wt%, assigned to the loss of coordinating water from two out of three Ni^{2+} cations, from 48 to 93 °C, and 2.1 wt%, assigned to water coordinating the last Ni^{2+} cation, from 93 to 148 °C (Supporting Information). From these data a composition of $Ni_2(H_2O)_2$**LL**·$9H_2O$ was proposed, which was found to be in reasonable agreement with elemental analysis data (expected, C = 21.6%, H = 6.6%, N = 4.2%; observed, C = 19.2%, H = 6.6%, N = 3.7%). N_2 adsorption was performed gravimetrically using a Hiden Isochema IGA gravimetric analyzer and indicated an uptake of 12.6 mmol g^{-1} (at $p/p_0 = 0.4$; Supporting Information). Further studies are ongoing to optimize the synthesis and activation conditions for STA-16(Ni).

The novel "honeycomb" STA-16 framework has the largest pore size of any reported crystalline metal phosphonate and represents the first example of isoreticular synthesis in the metal phosphonate family of compounds. The 1.8 nm free diameter of the channels—the largest one-dimensional channel of any known MOF—is comparable to the largest pore windows found in carboxylate MOFs with coordinatively unsaturated metal sites (MIL-101_NDC(Cr), 1.8 × 2.0 nm[4]). Removal of physisorbed water from the channels yields permanent porosity of 0.68 cm^3 g^{-1} (at $p/p_0 = 0.4$).

The structural features of the extra-large channels suggest possible applications in adsorption, storage, and release of large molecules or their catalytic conversion. The unique channel structure also suggests applications in the alignment of optically active molecules on a macroscopic scale, if larger crystals can be prepared.[25] It is likely that STA-16 will also be made with other divalent metal cations such as Mg^{2+}, Mn^{2+}, and Fe^{2+}, by analogy with experimental observation for STA-12 and the related carboxylate MOF CPO-27.[26,27] Upon dehydration of STA-16, the distorted octahedral coordination of the metal cations is thought to decrease to 5-fold coordination, due to the loss of one coordinating water molecule per cation, which leaves CUS accessible from the pores, with a concentration of 4.25 mmol g^{-1}. CUS offer potential binding sites for, for example, polyamines for enhanced CO_2 uptake or for drug molecules with appropriate functional groups to permit their controlled release.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis of the organic ligand, TGA data, structure refinement data, powder diffraction patterns before and after dehydration, and complete ref 6, as well as crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

paw2@st-andrews.ac.uk

ACKNOWLEDGMENT

We gratefully acknowledge the EPSRC (Project EP/F008384/1, M.T.W.) for funding, Prof. Chiu C. Tang for assistance at the I11 beamline at the Diamond Light Source (DLS), and DLS for beamtime.

REFERENCES

(1) Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Martinez, C.; Moliner, M. *Nature* **2006**, *443*, 842–845.

(2) Jiang, J.; Jorda, J.; Diaz-Cabanas, M.; Yu, J.; Corma, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 4986–4988.

(3) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040–2042.

(4) Sonnauer, A.; Hoffmann, F.; Fröba, M.; Kienle, L.; Duppel, V.; Thommes, M.; Serre, C.; Férey, G.; Stock, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 3791–3794.

(5) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523–527.

(6) Park, Y.; et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 8230–8233.

(7) Koh, K.; Wong-Foy, A.; Matzger, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 677–680.

(8) Férey, G. *J. Solid State Chem.* **2000**, *152*, 37–48.

(9) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714.

(10) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.

(11) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296–6301.

(12) Groves, J. A.; Miller, S. R.; Warrender, S. J.; Mellot-Draznieks, C.; Lightfoot, P.; Wright, P. A. *Chem. Commun.* **2006**, 3305–3307.

(13) Miller, S. R.; Pearce, G. M.; Wright, P. A.; Bonino, F.; Chavan, S.; Bordiga, S.; Margiolaki, I.; Guillou, N.; Férey, G.; Bourrelly, S.; Llewellyn, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 15967–15981.

(14) Pearce, G. M. Ph.D. Thesis, University of St Andrews, 2009.

(15) Alberti, G.; Costantino, U.; Marmottini, F.; Vivani, R.; Zappelli, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1357–1359.

(16) Clearfield, A.; Wang, Z. *J. Chem. Soc., Dalton Trans.* **2002**, 2937–2947.

(17) Gómez-Alcántara, M. D. M.; Cabeza, A.; Moreno-Real, L.; Aranda, M. A.; Clearfield, A. *Microporous Mesoporous Mater.* **2006**, *88*, 293–303.

(18) Mowat, J. P. S; Groves, J. A.; Wharmby, M. T.; Miller, S. R.; Li, Y.; Lightfoot, P.; Wright, P. A. *J. Solid State Chem.* **2009**, *182*, 2769–2778.

(19) Boultif, A.; Louer, D. *J. Appl. Crystallogr.* **2004**, *37*, 724–731.

(20) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory: Los Alamos, NM, 1994.

(21) Thompson, S. P.; Parker, J. E.; Potter, J.; Hill, T. P.; Birt, A.; Cobb, T. M.; Yuan, F.; Tang, C. C. *Rev. Sci. Instrum.* **2009**, *80*, 075107-9.

(22) Tarazona, P. *Phys. Rev. A* **1985**, *31*, 2672.

(23) Tarazona, P.; Marconi, U. M. B.; Evans, R. *Mol. Phys.* **1987**, *60*, 573–595.

(24) Jaroniec, M.; Kruk, M.; Oliver, J. P.; Koch, S. *Characterisation of Porous Solids V*; Proceedings of the 5th International Symposium on the Characterisation of Porous Solids (COPS-V); Elsevier: Amsterdam, 2000; Vol. 128, pp 71−80.

(25) Bruhwiler, D.; Calzaferri, G.; Torres, T.; Ramm, J. H.; Gartmann, N.; Dieu, L.; Lopez-Duarte, I.; Martinez-Diaz, M. V. *J. Mater. Chem.* **2009**, *19*, 8040–8067.

(26) Dietzel, P. D. C.; Johnsen, R. E.; Blom, R.; Fjellvåg, H. *Chem. Eur. J.* **2008**, *14*, 2389–2397.

(27) Dietzel, P. D. C.; Besikiotis, V.; Blom, R. *J. Mater. Chem.* **2009**, *19*, 7362–7370.