DOI: 10.1002/cctc.201402291



# Self-Assembled Hybrid Molybdenum Phosphonate Porous Nanomaterials and Their Catalytic Activity for the Synthesis of Benzimidazoles

Malay Pramanik and Asim Bhaumik\*<sup>[a]</sup>

A new porous organic–inorganic hybrid molybdenum phosphonate nanomaterial (HMoP-1) was synthesized through the reaction of benzene-1,3,5-triphosphonic acid and molybdenum(V) chloride under hydrothermal conditions in the absence of any structure-directing agent. The morphology of the hybrid material was found to be different at different synthesis temperatures. The material synthesized at 423 K (HMoP-1-LT) has spherical particle morphology, and the material synthesized at 453 K (HMoP-1-HT) has self-assembled flakelike morphology. Powder XRD, field-emission SEM, high-resolution TEM, N<sub>2</sub> sorption, solid-state <sup>13</sup>C cross-polarization magic-angle spinning NMR and <sup>31</sup>P magic-angle spinning NMR analyses, X-ray photoelectron spectroscopy, thermogravimetric differential thermal analysis, NH<sub>3</sub> temperature-programmed adsorption, and FTIR spectroscopic techniques were employed to characterize the samples and understand the morphological diversity. The orthorhombic crystal phase of the material was established through REFLEX and CELSIZ unit cell refinement programs. The calculated unit cell parameters of HMoP-1-HT are a=8.001(0.046) Å b=7.029 (0.039) Å, c=6.010 (0.036) Å; whereas HMoP-1-LT is amorphous in nature. HMoP-1-HT shows outstanding catalytic activity and high recycling efficiency for the green and efficient one-pot condensation reaction for the synthesis of bioactive 2-aryl benzimidazoles in excellent yields at room temperature.

# Introduction

Owing to the enhanced surface properties and structural diversity, the porous organic-inorganic hybrid materials have found huge potential applications in catalysis,<sup>[1]</sup> nanotechnology,<sup>[2]</sup> light harvesting,<sup>[3]</sup> chemical sensing,<sup>[4]</sup> gas storage,<sup>[5]</sup> separation,<sup>[6]</sup> and biomedical research.<sup>[7]</sup> Their design and synthesis have become an art to develop the next-generation functionalized solid-state materials. Thus, hybrid materials can provide an unmatched variety of structural motifs as potential building blocks for the development of extended porous solids.<sup>[8]</sup> Among the various types of open-framework porous nanomaterials invented to date, hybrid metal phosphonates are particularly interesting because of their versatility in potential applications.<sup>[9]</sup> Although research of this class of materials is under rapid development, the poor structural compatibility, and relatively lower ability of further processing of these organophosphonate-based porous hybrid materials, has restricted their engineering applications. The tetrahedral nature of the phosphonate group bearing oxygen atoms and very strong coordinative interaction with metal ion  $(M^{n+})$  makes the metal phosphonate chemistry more challenging when designing the open-framework hybrid architectures.<sup>[10]</sup> However, most of the porous metal phosphonates developed so far are predomi-

[a] M. Pramanik, Prof. Dr. A. Bhaumik Department of Materials Science Indian Association for the Cultivation of Science Jadavpur, Kolkata, 700 032 (India) E-mail: msab@iacs.res.in

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402291. nantly based on either linear mono- or diphosphonic acids as the organic spacer group. The thermal and mechanical stability of these materials are restricted because of limited cross-linking.<sup>[11]</sup> Thus, to enhance the cross-linking in the porous framework, by multidentate phosphonic acid sites of the ligand as the organic scaffold, we have introduced a triphosphonic acid (benzene-1,3,5-triphosphonic acid), inside the inorganic metal ions, to produce the porous organic-inorganic hybrid metal phosphonate materials.<sup>[12]</sup> In this context it is pertinent to mention that the synthesis and potential application of hybrid molybdenum phosphonates with an open framework structure remain of interest owing to their multidimensional structural features.<sup>[13]</sup> To date, most of the attention has been paid towards the synthesis of inorganic molybdenum phosphate and polyoxometalate materials having open-framework structures, and hybrid molybdenum phosphonate materials having unique structural diversity.<sup>[14]</sup> However, there are very few reports on the synthesis of organic-inorganic hybrid molybdenum phosphonate materials with an open framework structure<sup>[15]</sup> and their application based on surface properties.

The synthesis of substituted benzimidazoles has attracted huge research interest owing to its presence in a large number of natural products and pharmacologically active compounds.<sup>[16]</sup> Substituted benzimidazoles show a wide spectrum of pharmacological and biological properties, such as antiviral, antifungal, antimicrobial, anthelmintic, and anticancer activities.<sup>[17]</sup> More than five clinically important drug molecules, such as carbendazime, mebendazole, thiabendazole, pimozide, and omeprazole containing benzimidazole as the parent nucleus have been synthesized and extensively used worldwide.<sup>[18]</sup> Thus, a wide range of research activities have been focused on the design these compounds, specially through catalytic pathways involving microwave-assisted synthesis, solar thermal energies, Lewis acid catalysis, and solid-supported homogeneous catalysis to increase the product yield and minimize the reaction time and temperature.<sup>[19]</sup> However, many of these methods have several drawbacks, such as long reaction time, high reaction temperature, leaching of the metal ions, and expensive reagents. In some cases, 2-substituted and 1,2-disubstituted benzimidazole were generated simultaneously with poor selectivity.<sup>[19]</sup> Thus, a green and eco-friendly methodology for the production of 2-aryl benzimidazole is highly desirable.

Herein, we report a new supermicroporous molybdenum phosphonate material with high BET surface area and crystalline novel open-framework structure. The conversion from noncrystalline nanoparticles into crystalline flakelike morphology was achieved very efficiently by changing the reaction temperature. Furthermore, porous organic-inorganic hybrid materials with positively charged metal ion (Mo<sup>5+</sup>) at higher oxidation state can play a crucial role as a nanoreactor to conduct the condensation reaction involving two or more reactant molecules with desired selectivity.<sup>[20]</sup> This hybrid molybdenum phosphonate material showed excellent catalytic properties for the one-pot synthesis of 2-aryl benzimidazoles through the condensation reaction of o-phenylenediamine and substituted aromatic aldehydes at room temperature within 30 min reaction time. To the best of our knowledge, this is the first report of organic-inorganic hybrid molybdenum phosphonate with open-framework structure and its potential as a nanoreactor for the synthesis of 2-arylbenzimidazoles, which could eliminate the drastic and hazardous reaction conditions, such as the use of hazardous organic solvents, reactants, high reaction temperature, and long reaction time. The hybrid molybdenum phosphonate catalyst can be easily separated through simple filtration and can be reused five times without significant loss of its catalytic activity.

# **Results and Discussion**

# Mesophase and nanostructure

The small-angle XRD pattern for HMoP-1-HT is shown in Figure 1. As seen from the figure, this hybrid molybdenum phosphonate material has one broad peak corresponding to the mesophase at  $2\theta = 2.56^{\circ}$ . This could be attributed to the presence of disordered mesophase as a result of the self-assembly of nanoparticles.<sup>[12,21]</sup> The interparticle distance corresponding to the small-angle peak is 3.4 nm, suggesting that the nanostructure of HMoP-1-HT is generated by the self-assembly of very tiny nanoparticles. However, for HMoP-1-LT sample no such peak was observed in the small-angle XRD pattern (see the Supporting Information, Figure S1). This result suggests that at lower hydrothermal temperature, the self-assembled nanostructure/mesophase is not formed. The wide-angle X-ray diffraction pattern of the HMoP-1-HT sample is shown in Figure 2. At lower hydrothermal temperature (423 K),



Figure 1. Small-angle powder XRD pattern of HMoP-1-HT.



Figure 2. Wide-angle powder XRD pattern of HMoP-1-HT. Difference between experimental and theoretical PXRD pattern is shown in the inset.

the coordination between all the three phosphonic acid of the organophosphonate precursor molecule and molybdenum is less and the crystallization does not take place properly; as a consequence the 3D network cannot crystallize. As a result, the material HMoP-1-LT is amorphous in nature (inset of Figure S1). However, at higher hydrothermal temperature (453 K), proper coordination and crystallization takes place and a crystalline 3D porous network was formed with open framework structure.<sup>[22]</sup> The wide-angle powder XRD (PXRD) pattern of the material (HMoP-1-HT) did not match with any crystalline phase previously reported in the JCPDS database. Thus, the crystal structure of HMoP-1-HT was evaluated from the experimental PXRD pattern with REFLEX software. The extent of matching between the theoretical wide-angle XRD and experimental PXRD was verified by CELSIZ unit cell refinement program (inset of Figure 2). The diffraction peaks could be assigned as a new orthorhombic crystal phase and the corresponding crystal parameters are a = 8.001(0.046) Å, b = 7.029 (0.039) Å, c =6.010 (0.036) Å. The unit-cell volume ( $V = 338.332 \text{ Å}^3$ ) together with the very low standard deviation (ESD = 3.411) is in good agreement with the predicted crystal parameters and the actual crystal structure. The unit-cell parameters with standard deviations are given in Table 1 and the corresponding Miller indices for the different planes of the material (HMoP-1-HT) are

# CHEMCATCHEM FULL PAPERS

Table 1. Crystal parameters of HMoP-1-HT.					
Chemical formula Formula weight [g mol <sup>-1</sup> ]	C <sub>6</sub> H <sub>3</sub> P <sub>3</sub> O <sub>9</sub> Mo <sub>1.8</sub> 488.13				
Symmetry	orthorhombic				
Lattice parameters	<i>a</i> =8.001 (0.046) Å <i>b</i> =7.029 (0.039) Å <i>c</i> =6.010 (0.036) Å				
Volume (ESD)	V=338.332 (3.411) Å <sup>3</sup>				
Wavelength [Å]	1.5406				
Range of data collection	$10 \leq 2\theta \leq 70$				
Angular step [°]	0.02 (ω)				
Time per step [s]	25				

Table 2	. Indexing of ort	horhombic cryst	al phase of HMoP-1-H	T.
h	k	1	20	d
1	0	0	11.635	7.605
0	1	0	12.590	7.030
0	0	1	13.058	6.779
1	1	0	16.615	5.335
0	1	1	19.611	4.526
1	0	1	20.298	4.374
2	0	0	22.874	3.887
1	1	1	23.949	3.715
1	2	0	28.347	3.148
0	2	1	29.311	3.046
1	2	1	31.666	2.825
3	0	0	33.072	2.708
3	1	0	35.584	2.522
0	3	1	41.704	2.165
3	2	0	42.204	2.141
2	3	0	44.225	2.047
1	0	3	46.820	1.940
1	1	3	48.217	1.887
0	3	2	49.186	1.852
1	4	1	55.762	1.648
2	2	3	58.136	1.586
5	0	1	60.199	1.537
5	1	1	61.375	1.510
1	4	2	62.332	1.489
3	4	1	65.202	1.430
1	2	4	69.174	1.358

listed in Table 2. Observed and calculated d spacing corresponding to a given plane are in very close agreement.

As the hydrothermal synthesis temperature decreases, the particle size of the hybrid molybdenum phosphonate (HMoP-1-LT) increases (observable from electron-microscopy analysis, see below), different from the behavior of the material synthesized at higher temperature (HMoP-1-HT). From the thermodynamics point of view this can be explained by the fact that as the particle size of the nanoparticle increases, the tendency of self-assembly decreases gradually.<sup>[23]</sup> Thus the HMoP-1-HT nanoparticles are susceptible for self-assembly to form the respective mesophase. On the other hand, in the case of HMoP-1-LT, owing to its comparatively bigger particle sizes and their amorphous nature, the self-assembly process is prohibited (Scheme 1).



**Scheme 1.** Probable mechanistic pathway for the formation of hybrid nanoparticles and nanoflakes at different temperatures.

#### **Electron microscopic analysis**

The characteristic high-resolution TEM (HRTEM) images of the molybdenum phosphonate sample HMoP-1-LT are shown in Figure S2a and S2b. As seen from the images, this low-temperature-synthesized material possesses uniform spherical particle morphology (particle size  $\approx$  45–50 nm). The representative HRTEM images of the HMoP-1-HT sample are shown in Figure S2c. The closer view of the image reveals the self-assembled unsymmetrical flakelike morphology of the material with dimension of approximately 150-155 nm. The flakes have a hierarchical structure that is generated by the self-assembling of nanoparticles of dimension of approximately 16-18 nm. Furthermore, the closer view of an individual particle reveals a nanoflake-like morphology (Figure S2d). These nanoparticles are generated by the self-assembling of very tiny nanospheres (dimension  $\approx$  3–4 nm). This self-assembled nanostructure is the origin of one broad small-angle X-ray diffraction peak of HMoP-1-HT as shown in Figure 1. The uniform white spots of dimension of approximately 1.6 nm throughout the individual nanoflake (Figure S2d) are the signature of the presence of the supermicropores in the material. The supermicropores could be attributed to the cross-linking between metal and benzene-1,3,5-triphosphonic acid bearing three phosphonic acid groups. The clear crystal fringes are also observable from the HRTEM image (Figure S3) of HMoP-1-HT. The representative SEM images of the material HMoP-1-LT are shown in Figure 3a and 3b. The finely monodispersed nanoparticles with dimensions of approximately 45 nm are spread throughout the specimen. The flakelike morphology with a dimension of approximately 150-160 nm is clearly observable for the sample HMoP-1-HT; as shown in Figure 3 c. A closer view of the SEM image (Figure 3 d) of HMoP-1-HT reveals that every flake was generated by the assembly of very tiny nanospheres.

### BET surface area and porosity

The permanent architectural porosity of hybrid molybdenum phosphonate nanomaterials has been determined through  $N_2$  adsorption–desorption analysis at liquid  $N_2$  temperature and the results are shown in Figure 4. The pore size of the materials was calculated by means of nonlocal density functional theory (NLDFT) and the results are shown in Figure 5. The BET

# CHEMCATCHEM FULL PAPERS



Figure 3. Field-emission SEM image of a, b) HMoP-1-LT and c, d) HMoP-1-HT.



Figure 4. N<sub>2</sub> adsorption and desorption isotherms for HMoP-1-HT and HMoP-1-LT at 77 K. Adsorption points are marked by filled circles and triangles, desorption points by empty circles and triangles.



Figure 5. NLDFT pore-size distribution for HMoP-1-HT (filled circles) and HMoP-1-LT (filled triangles).

surface area of HMoP-1-HT is 183 m<sup>2</sup>g<sup>-1</sup> with a corresponding pore volume of 0.148 cm<sup>3</sup>g<sup>-1</sup>. The isotherm for HMoP-1-HT can be classified as a mixture of type I and IV isotherms according to standard IUPAC nomenclature.<sup>[24]</sup> Furthermore, in the intermediate relative pressure region ( $P/P_0 = 0.1-0.6$ ), the N<sub>2</sub> adsorption amount increases gradually, a characteristic of multilayer adsorption and the presence of a considerable amount of mesopores in the material.<sup>[25]</sup> Moreover, at higher relative pressure  $(P/P_0 > 0.75)$  the amounts of N<sub>2</sub> adsorption increase greatly, suggesting the presence of interparticle porosity in HMoP-1-HT. The desorption isotherm of the material does not show any hysteresis loop. Further, the t-method micropore analysis revealed that the material consists of an internal micropore area of 122 m<sup>2</sup>g<sup>-1</sup> together with an external mesopore area of 61 m<sup>2</sup>g<sup>-1</sup>. The corresponding micropore and mesopore volume is  $8 \times 10^{-2}$  cm<sup>3</sup> g<sup>-1</sup> and  $6 \times 10^{-2}$  cm<sup>3</sup> g<sup>-1</sup>, respectively. The NLDFT pore-size distribution of the material further suggests that the HMoP-1-HT material is composed of two types of pores having the dimension of approximately 1.6 and 2.7 nm, respectively. The supermicroporosity of the material was generated by 3D cross-linking within the open-framework structure between organophosphonic acid ligand and molybdenum, and the mesoporosity (2.7 nm) of the material could be originated by the self-assembly of hybrid nanoparticles (observable from both the SEM and TEM analysis). On the other hand, the isotherm for material HMoP-1-LT points to a nonporous nature with a BET surface area of only 32 m<sup>2</sup>g<sup>-1</sup> and a pore volume of  $2 \times 10^{-2} \, \text{cm}^3 \text{g}^{-1}.$  This nonporous nature is probably the result of insufficient cross-linking between the metal and organophosphonic acid ligand at lower hydrothermal temperature (423 K). Hence, owing to the ineffective 3D cross-linking and lack of crystallization at low temperature in HMoP-1-LT, the internal surface area of the material is lower than that of the material synthesized at higher temperature (453 K).

### Thermal analysis

The thermal stability of the hybrid molybdenum phosphonate HMoP-1-HT was examined by using thermogravimetric analysis under N<sub>2</sub> atmosphere with a heating rate of  $10^{\circ}$ C min<sup>-1</sup> (Figure S4). The material exhibits two-step mass losses of total 37.8 wt% through the temperature interval 298–800 K. The first 11.85 wt% endothermic weight loss is assigned to the loss of adsorbed water molecule present at the surface of the porous framework. The second 25.95 wt% exothermic mass loss is probably caused by the breaking of C–C and C–P bonds during burning of the organic framework. High exothermic peak maxima at 773 K suggested very high stability of the hybrid molybdenum phosphonate framework. Thus, from the thermal analysis data it can be suggested that the porous molybdenum(V) phosphonate material HMoP-1-HT has considerably good thermal stability.

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

# CHEMCATCHEM FULL PAPERS

# Bonding and framework structure

The FTIR spectrum of HMoP-1-HT was shown in Figure S5. The peak at 547 cm<sup>-1</sup> could be assigned for the characteristic stretching vibration of the Mo-O bond. The broad peak centered at 1025 cm<sup>-1</sup> could be assigned to the stretching vibration of the tetrahedral CPO<sub>3</sub> group. The presence of benzene ring in the porous framework is confirmed by the characteristic stretching vibration at 1405 cm<sup>-1</sup>. The peak at 1630 cm<sup>-1</sup> is responsible for bending vibration of adsorbed water molecules in the porous framework. The broad peak centered at 3427 and 3203 cm<sup>-1</sup> is probably caused by the free adsorbed water molecule and free P-OH groups in the porous framework. Thus the FTIR spectroscopic result suggest the presence of benzene-1,3,5-triphosphonic acid in the porous architecture. The absence of peaks at 961 cm<sup>-1</sup> and 1385 cm<sup>-1</sup> signifies that the material does not contain any M=O<sup>t</sup> (O<sup>t</sup> = terminal oxo group) and P=O in the framework.<sup>[26]</sup>

# Solid-state magic-angle spinning NMR studies

Solid state <sup>13</sup>C cross-polarization magic-angle spinning NMR (<sup>13</sup>C CP–MAS–NMR) and <sup>31</sup>P magic-angle spinning NMR (<sup>31</sup>P MAS–NMR) experiments generally provide information about the chemical environment around C and P nuclei in the hybrid metal phosphonate framework. In Figure 6, the <sup>13</sup>C CP–



Figure 6. <sup>13</sup>C CP-MAS-NMR spectrum of HMoP-1-HT.

MAS–NMR spectrum of HMoP-1-HT is shown. It exhibits two peaks at 131.6 and 135.4 ppm with almost similar intensity, indicating the presence of two types of carbon with equal number of atoms (shown in the inset of Figure 6). On the other hand, the <sup>31</sup>P MAS–NMR spectrum of HMoP-1-HT sample (Figure 7) displays one strong signal at 11.9 and a very weak one at 18.5 ppm. These signals could be attributed to the  $[(OMo)_3P]_3-C_6H_3$  and  $[(OH)(OMo)_2P]_3-C_6H_3$  species, respectively. These spectroscopic results further suggest the presence of organic fragment ( $C_6PO_3H_3$ ) in the porous molybdenum(V) phosphonate framework of HMOP-1-HT.<sup>[27]</sup>





Figure 7. <sup>31</sup>P MAS–NMR spectrum of HMoP-1-HT.

# UV/Vis diffuse reflectance spectroscopy

The solid state UV/Vis reflectance spectroscopy is a very important characterization tool to confirm the oxidation state of the central metal ion in the organic–inorganic hybrid materials. The UV/Vis reflectance spectra for the HMoP-1-HT, HMoP-1-LT, and HMoP-1-HT (after catalysis) are shown in Figure 8. For



**Figure 8.** UV/Vis reflectance spectra of HMoP-1-HT, HMoP-1-LT, and HMoP-1-HT (after catalysis).

HMoP-1-HT, the absorption band at 744–834 nm is related to  $Mo^{5+}$  ions to the hybrid phosphonate framework.<sup>[28]</sup> The characteristic peak of  $Mo^{5+}$  is also observable at 401 nm and attributed to the  ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$  transition.<sup>[29]</sup> The peak centered at 260 nm could be attributed to the presence of chromophoric phenyl group in the porous hybrid framework. The high-energy absorption peak at 214 nm could be attributed to the charge transfer from oxygen atom to molybdenum(V) atoms.<sup>[30]</sup> After the catalytic reaction, the UV/Vis diffuse reflectance spectrum of HMoP-1-HT does not alter, which indicates that the structural environment and oxidation state of molybdenum remain unaltered after catalysis. For HMoP-1-LT, the absence of peaks in the lower energy region (600–900 nm) indicates the presence of Mo<sup>6+</sup> ions in the framework.<sup>[30]</sup> The large intensity of the high-energy absorption peak at approximately 218 nm also

suggests the strong charge transfer interaction between oxygen atom to molybdenum(VI) atoms. The red-shifting of the charge-transfer spectrum of HMoP-1-LT relative to that of HMoP-1-HT is also a good indication of the higher oxidation state of Mo in HMoP-1-LT.

### Molecular formula of HMoP-1-HT

Thermogravimetric differential thermal analysis (TG-DTA) of the sample HMoP-1-HT indicates the presence of 25.9 wt% organics in the material. On the other hand, the CHN analysis data suggest the presence of 14.8 wt% carbon and 1.8 wt% hydrogen in this porous framework. Furthermore, inductively coupled plasma atomic emission spectroscopy (ICP-AES) studies reveal the presence of 41.6 wt% molybdenum in HMoP-1-HT. Furthermore, the energy-dispersive spectrometry (EDS) analysis of the sample reveals the presence of 18.86 wt% phosphorus. Thus, the molar ratio of C/Mo/P = 2.05:0.72:1 is in good agreement with the calculated C/P molar ratio of 2:1 in the synthesized organophosphorous ligand (benzene-1,3,5-triphosphonic acid). From the FTIR and solid-state <sup>13</sup>C CP-MAS-NMR and <sup>31</sup>P MAS–NMR study, also the presence of benzene-1,3,5-triphosphonic acid in the porous framework is confirmed. Thus, probable molecular formula of the porous architecture of HMoP-1-HT can be written as  $C_6P_3O_9Mo_{1.8}$ ,  $Mo_{0.46}O_{x}$ ,  $yH_2O$ .

#### X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) has proven to be not only a powerful scientific tool for investigating the electronic structure in solids but also utilized in the analysis of composition, bonding, and local structure of the material. The XPS survey spectrum of the HMoP-1-HT and HMoP-1-LT material reveals the presence of elements, such as oxygen, molybdenum, carbon, and phosphorus (Figure 9). The HMoP-1-HT material shows the major peaks at 135.03, 192.47, 235.01, 287.34, 399.62, 416.89, 532.61, and 744.91 eV, which corresponds to P2p, P2s, Mo3d, C1s, Mo3p<sub>3/2</sub>, Mo3p<sub>1/2</sub>, O1s, and OKLL peaks, respectively [OKLL: the energy of the electrons ejected from the atoms due to the filling of the O1s state (K shell) by an



Figure 9. XPS survey curve of HMoP-1-HT and HMoP-1-LT.



**Figure 10.** High resolution XPS for a) Mo 3d and b) Mo 3p orbitals of HMoP-1-HT, HmoP-1-LT, and HMoP-1-HT (after catalysis).

electron of the L shell coupled with the ejection of an electron from L shell]. After high-resolution XPS, the Mo spectrum of HMOP-1-HT for 3d orbitals (Figure 10a) contains two peaks at 233.70 and 236.80 eV for Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub>, respectively, whereas for HMoP-1-LT the peaks are observed at 234.68 and 237.82 eV, respectively. The results signify the presence of Mo<sup>5+</sup> in HMoP-1-HT and Mo<sup>6+</sup> in HMoP-1-LT.<sup>[31]</sup> The high-resolution spectra for 3p orbitals of Mo in both materials contain two well-resolved peaks at 399.62 and 416.89 eV for HMoP-1-HT, and at 400.67 and 418.03 eV for HMoP-1-LT, respectively. These peaks are responsible for  $Mo 3p_{3/2}$  and  $Mo p_{1/2}$  of  $Mo^{5+}$ and Mo<sup>6+</sup> moiety in the porous hybrid material of HMoP-1-HT and HMoP-1-LT, respectively. (Figure 10b) For HMoP-1-HT, the peak at 286.32 eV is caused by the presence of sp<sup>2</sup> hybridized carbon in the porous material. (Figure S6a) The peaks at 135.03 and 192.47 eV is caused by the presence of P2p and P2s in the hybrid material (Figure S6b and S6c). The broad peak centered at 532.61 eV is assigned to the O1s of the material (Figure S6d). The broadening of the peak is caused by the presence of two types of oxygen atoms in the material, bridging and nonbridging oxygen atoms towards the metal ion.<sup>[32]</sup> Quantification of the elements present in the material through XPS analysis suggests the presence of elements in the ratio C/ P/Mo/O = 2.08:1:0.76:8.64. Hence, the molecular formula of the material (HMoP-1-HT) is  $C_6P_3O_9Mo_{1.8}$ ,  $Mo_{0.48}O_{x}$ ,  $yH_2O(x+y=$ 16.92), which almost completely matches with the chemical

 $<sup>\</sup>ensuremath{^{\odot}}$  2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

formula extracted from the other (TG–DTA, ICP–AES, and EDS) experimental results. The XPS survey spectrum of the HMoP-1-LT material reveals the presence of elements, such as carbon, phosphorus, molybdenum, and oxygen (Figure 9) in the ratio of C/P/Mo/O = 1.98:1:0.72:9.23. Hence, the molecular formula of HMoP-1-LT is C<sub>6</sub>P<sub>3</sub>O<sub>9</sub>Mo<sub>1.5</sub>, Mo<sub>0.66</sub>O<sub>x</sub>, yH<sub>2</sub>O (x+y=18.69). From the high-resolution XPS spectrum (Figure 10 a and b) it is clear that after catalysis the oxidation state of Mo does not change, which also supports our previous results of UV/Vis diffuse reflectance spectra.

#### Temperature-programmed desorption analysis

Temperature-programmed desorption (TPD) of ammonia was measured to evaluate the total acidity and strength of the acid sites in the porous molybdenum phosphonate material. The desorption of ammonia started at very low temperature (Figure 11). Two broad peaks with low intensity at approxi-



Figure 11. NH<sub>3</sub> TPD profile of HMoP-1-HT.

mately 326 and 417 K, respectively, are probably caused by the weakly adsorbed NH<sub>3</sub> to the Lewis and Bronsted acid sites of the porous matrix (HMoP-1-HT). As the temperature increases, one intense peak is observed at 595 K, which is probably responsible for the highly acidic Bronsted sites of the material.<sup>[33]</sup> The Lewis acidity of the material arises as a result of the presence of Mo in the hybrid material and the Bronsted acidity of the material is generated by the presence of free -P(OH) groups in the porous material. The total acidity evaluated from the NH<sub>3</sub>-TDP analysis of the material (HMoP-1-HT) is 1.45 mmolg<sup>-1</sup>.

Such a material with high surface acidity can be used as a catalyst for the condensation reaction at ambient temperature.

#### Catalysis over HMoP-1

The porous hybrid molybdenum phosphonate material was used as a catalyst for the selective one-pot synthesis of 2-arylbenzimidazoles at room temperature (Scheme 2) by the con-





Scheme 2. Reaction pathway for the formation of 2-arylbenzimidazole.

Entry	R	Product	Yield [%] <sup>[b</sup>
1	Ph		93
2	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		95
3	p-BrC <sub>6</sub> H <sub>4</sub>	N N N Br	90
4	p-CIC <sub>6</sub> H <sub>4</sub>		91
5	p-FC <sub>6</sub> H <sub>4</sub>		93
6	2-thiophenyl	N S	86
7	m-BrC <sub>6</sub> H <sub>4</sub>	N	87
8	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		92
9 <sup>[c]</sup>	Ph		62
10 <sup>[d]</sup>	Ph		53
11 <sup>[e]</sup>	Ph		40
12 <sup>[f]</sup>	Ph		-
[a] Reactie (1 mmol) hyde; rea ucts were	on conditions: al ; 5 wt% catalyst HM action temperature = e characterized by <sup>1</sup> H	dehyde (1 mmol); 1,2-phe pP-1-HT with respect to corre 298 K; reaction time = 30 mi and <sup>13</sup> C NMR spectra and yie	enylenediamin sponding alde n. [b] All proc ld refers to isc

ucts were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra and yield refers to isolated products. [c] Reaction was performed with 5 wt% HMoP-1-LT as the catalyst. [d] Reaction was performed with  $H_3PO_4$  as the catalyst. [e] Reaction was performed with  $MoCl_5$  as the catalyst. [f] Reaction was performed in the absence of any catalyst.

densation of *o*-phenylenediamine and substituted aromatic aldehydes (Table 3). The yield of the 2-aryl benzimidazole products were measured by weighing the final products and these compounds were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see the Supporting Information). The electron-donating or -withdrawing groups in the substituted aldehydes do not hamper the product yield; keeping this in mind we proposed a reaction mechanism for the formation of 2-arylbenzimidazole over HMoP-1 as shown in Scheme 3 (only Lewis acidic sites are



**Scheme 3.** Probable reaction mechanism and catalytic role of HMoP-1-HT in the selective synthesis of 2-arylbenzimidazoles.

represented for clear imaging). In this reaction mechanism, the molybdenum(V) with vacant d orbitals in the porous hybrid framework and free -P(OH) groups in the material play the crucial role for activating the carbonyl carbon of the substituted aldehydes. The molybdenum(V) or free -P(OH) generate a high electrophilicity in the carbonyl carbon of the aldehyde. We synthesized two types of hybrid molybdenum phosphonate materials HMoP-1-HT and HMoP-1-LT to check the effect of surface area and morphology on the catalytic performance for the synthesis of 2-arylbenzimidazole with benzaldehyde as a reference carbonyl compound. The yield of 2-phenylbenzimidazole was only 62% if HMoP-1-LT (BET surface area 32 m<sup>2</sup>g<sup>-1</sup>) was used as a catalyst but the yield largely increased to 93% if HMoP-1-HT (BET surface area =  $183 \text{ m}^2\text{g}^{-1}$ ) was the catalyst. As the surface area of the catalysts decreased, the mass transport through the porous channel was largely prohibited, which is reflected in the isolated yield of the product. Moreover, as the particle size decreased, the number and uniformity of the active catalytic sites (here Mo<sup>V</sup>) increased gradually; this effect is also responsible for the higher catalytic efficiency of HMoP-1-HT (particle size  $\approx$  3–4 nm) over HMoP-1-LT (particle size 45– 50 nm).<sup>[34]</sup> If the reaction was performed in the absence of any catalyst, no benzimidazole product was isolated even after prolonged reaction time. In this context we performed a reaction by using MoCl<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub> as the catalysts and isolated benzimidazole in 40% and 53% yield. There are few iron(III)-containing homogeneous and heterogeneous catalysts that are also used as catalysts for the production of benzimidazole but the yield is very low and the reaction time and temperature are high<sup>[35]</sup> compared with the conditions for our reported HMoP-



Scheme 4. Reaction pathway for the formation Hantzsh ester.

<b>Table 4.</b> Recycling efficiency of the catalyst HMoP-1-HT for the synthesis of 2- arylbenzimidazole. <sup>[a]</sup>								
Cycle number	1	2	3	4	5			
Yield [%]	93.0	92.4	91.8	90.7	89.8			
[a] Reaction conditions: aldehyde (1 mmol), 1,2-phenylenediamine (1 mmol), 5 wt% catalyst HMoP-1-HT with respect to the corresponding aldehyde reaction temperature = 298 K reaction time = 30 min								

1-HT catalyst. To demonstrate the highly acid catalytic activity of the material (HMoP-1-HT), we also performed one another catalytic reaction, Hantzsh ester synthesis (Scheme 4) in ethanol at 333 K.<sup>[36]</sup> The corresponding results are listed in Table 5, suggesting a high yield of the product 1,4-dihydropyridine. This result suggested that HMoP-1-HT can be employed as an efficient acid catalyst for a wide range of organic reactions.

#### Recycling efficiency of the catalyst

The catalyst was recovered from the reaction mixture by filtration and was washed with methanol and acetone repeatedly to remove the polar and nonpolar substrates from the surface of the catalyst (HMoP-1-HT). Before the recycling test, the catalyst was dried overnight at 333 K and the procedure was repeated for five times (Figure S7). The reusability of the catalyst was tested by using benzaldehyde as the reference carbonyl compound (Table 4). As seen from Figure S7 the product yields were very consistent suggesting high catalytic efficiency of HMoP-1-HT in the synthesis of 2-arylbenzimidazoles. Furthermore, to test whether any metal (Mo) or organics (benzene-1,3,5-triphosphonic acid) are leached out from HMoP-1-HT during the reaction, in one reaction cycle the catalyst was separated from the reaction mixture after 25 min through filtration. At this stage, the yield of the product was 71%. Then the reaction was continued without the catalyst at room temperature for another 5 h. After 5 h the product was analyzed and the conversion was found to increase by a very insignificant amount (yield 71.5%). This result confirms that during the catalytic reaction no leaching of the catalyst takes place and the catalytic pathway is completely heterogeneous in nature.

# Conclusions

We report a highly crystalline new organic–inorganic hybrid porous molybdenum(V) phosphonate material by using benzene-1,3,5-triphosphonic acid as an organic scaffold under hydrothermal condition. Nanoparticles and agglomerated flakelike morphology of the materials were obtained simply by tuning the hydrothermal synthesis temperature. The hybrid phosphonate material HMOP-1-HT showed high surface area and uniform supermicropores and mesopores. This porous hybrid material was utilized as an efficient catalyst for the synthesis of biologically important value-added 2-arylbenzimidazoles through one-pot condensation reaction under green and mild reaction conditions. A wide variety of commercially available important drug molecules contain 2-arylbenzimidazoles or

# CHEMCATCHEM Full papers



1,4-dihydropyridines as a parent nucleus. Thus, our novel hybrid HMoP-1-HT catalyst has huge potential to be explored for selective synthesis of bioactive molecules, such as substituted 2-arylbenzimidazoles and 1,4-dihydropyridines. The novel porous nanocatalyst developed herein may open up new avenues in the synthesis of organic fine chemicals under ecofriendly conditions.

# **Experimental Section**

# Materials

Commercially available 1,3,5-tribromobenzene (98%), triethyl phosphite (98%), molybdenum(V) chloride (95%), and 1,3-diisopropylbenzene were purchased from Sigma–Aldrich. Anhydrous Nickel(II) bromide (99%) were purchased from Avra Chemicals.

# Synthesis of benzene-1,3,5-triphosphonic acid

Benzene-1,3,5-triphosphonic acid was prepared by the previously reported procedure.<sup>[37]</sup> The compound was characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR, and IR spectroscopy. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  = 8.07 ppm (t, 3*J*PH) 15 Hz); <sup>13</sup>C NMR (500 MHz, D<sub>2</sub>O):  $\delta$  = 135.23; 136.07 ppm; <sup>31</sup>P NMR (500 MHz, D<sub>2</sub>O):  $\delta$  = 12.87 ppm. IR (KBr):  $\tilde{\nu}$  = 3387, 3088, 2925, 2319, 1142, 1001, 943, 691, 536, 470 cm<sup>-1</sup>.

#### Synthesis of the porous molybdenum(V) phosphonate

In the typical synthesis of hybrid molybdenum phosphonate, benzene-1,3,5-triphosphonic acid (1.90 g, 6 mmol) was dissolved into a water–ethanol (1:1) mixture (40 mL). In another beaker, molybdenum(V) chloride (2.94 gm, 10.8 mmol) was dissolved into dry ethanol (30 mL) separately. The synthetic gel was prepared by the dropwise addition of the phosphonic acid solution to the ethanolic metal salt solution within 1 h under vigorous stirring condition. After 2–3 h, the pH of the synthetic gel was increased by 4 by addition of 12.5% aqueous ammonia solution. The deep greenish color gel was further stirred overnight and transferred to two Teflon lined pressure vessel and kept at 453 K and 423 K for 24 h. The Teflon leaned autoclaves were cooled to RT very slowly (10 °Ch<sup>-1</sup>). The materials were isolated by filtration with repeated washing by water and ethanol. The materials, namely HMOP-1-HT (hydrothermal temperature 453 K) and HMOP-1-LT (hydrothermal temperature 423 K) were dried under vacuum desiccators.

#### Instrumentation

PXRD patterns were recorded on a Bruker d-8 Advance diffractometer operated at 40 kV and 40 mA and calibrated with a standard silicon sample, using Ni-filtered Cu<sub>Ka</sub>  $(\lambda = 0.15406$  nm). JEOL JEM6700F field-emission scanning electron microscope was used for the determination of the morphology of powder samples. The pore structure was explained by a JEOL JEM2010 transmission electron

microscope operated at an accelerating voltage of 200 kV.  $N_{\rm 2}$  adsorption/desorption isotherms of the samples were recorded on a Quantachrome Autosorb 1-C/TPD, at 77 K. Prior to the measurements, the samples were degassed at 423 K for 12 h under high vacuum. UV/Vis diffuse reflectance spectra were obtained by using a Shimadzu UV 2401PC spectrophotometer with an integrating sphere attachment. BaSO<sub>4</sub> pellet was used as a background standard. FTIR spectra were recorded by using a Nicolet MAGNA-FT IR750 Spectrometer Series II. <sup>1</sup>H NMR and <sup>13</sup>C experiments were performed on a Bruker DPX-300 NMR spectrometer. TGA and DTA of the samples were performed in a TGA instrument thermal analyzer TA-SDT Q-600 under N<sub>2</sub> flow. XPS was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic  $\text{Al}_{K\alpha}$  X-ray source. TPD–NH3 was performed in a Micromeritics Instrument Corporation ChemiSorb 2720 pulse chemisorption system.

# **Catalytic reactions**

In the typical catalytic reaction, a 10 mL round bottom flask was charged with *o*-phenylenediamine (1 mmol), various substituted aldehydes (1 mmol), and 5 wt% HMoP-1-HT in ethanol (5 mL) at RT. The whole mixture was stirred well with a magnetic stirrer for 30 min. After the confirmation of the final product through thin layer chromatography, the reaction mixture was filtered and the catalyst was washed with ethanol. The crude product was isolated by vacuum evaporation of the ethanolic solution. The crude product was diluted with  $CH_2Cl_2$  and washed with brine solution repeatedly and dried over anhydrous  $Na_2SO_4$ . The pure products were collected by vacuum evaporation of the organic part. The yield of the products was confirmed by weighing and the purity was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy data.

# Acknowledgements

MP wishes to thank CSIR, New Delhi for Senior Research Fellowships. AB wishes to thank DST, New Delhi for instrumental support through DST Unit on Nanoscience and DST-SERB project grants.

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**Keywords:** heterocycles · mesophases · molybdenum organic–inorganic hybrid composites · self-assembly

- [1] a) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu, J. Am. Chem. Soc.
   2012, 134, 87–90; b) A. Corma, U. Diaz, T. Garcia, G. Sastre, A. Velty, J. Am. Chem. Soc. 2010, 132, 15011–15021.
- [2] a) C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millan, V. S. Amaral, F. Palacio,
   L. D. Carlos, *J. Lumin.* **2013**, *133*, 230–232; b) T. Govindaraju, *Nanoscale* **2012**, *4*, 6102–6117; c) H. S. Huang, K. H. Chang, N. Suzuki, Y. Yamauchi,
   C. C. Hu, K. C. W. Wu, *Small* **2013**, *9*, 2520–2526.
- [3] M. Waki, N. Mizoshita, Y. Maegawa, T. Hasegawa, T. Tani, T. Shimada, S. Inagaki, *Chem. Eur. J.* **2012**, *18*, 1992–1998.
- [4] a) A. A. Khan, L. Paquiza, A. Khan, J. Mater. Sci. 2010, 45, 3610–3625;
   b) T. H. T. Thi, R. Dagnelie, S. Crunaireza, L. Nicole, Chem. Soc. Rev. 2011, 40, 621–639.
- [5] a) Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe, B. Chen, *Angew. Chem. Int. Ed.* 2011, *50*, 3178–3181;
   *Angew. Chem.* 2011, *123*, 3236–3239; b) S. B. Kalidindi, H. Oh, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo, R. A. Fischer, *Chem. Eur. J.* 2012, *18*, 10848–10856.
- [6] a) J. C. Hicks, J. H. Drese, D. J. Fauth, M. L. Gray, G. Qi, C. W. Jones, J. Am. Chem. Soc. 2008, 130, 2902–2903; b) J. H. Chang, S. Y. Lee, J. Lee, Curr. Org. Chem. DOI: 10.2174/1385272811317100003.
- [7] a) E. Ruiz-Hitzky, M. Darder, P. Aranda, K. Ariga, Adv. Mater. 2010, 22, 323–336; b) X. Bi, H. Zhang, T. Fan, CN102580640A, 2012.
- [8] a) Y. Yamauchi, N. Suzuki, P. Gupta, K. Sato, N. Fukata, M. Murakami, T. Shimizu, S. Inoue, T. Kimura, *Sci. Technol. Adv. Mater.* 2009, *10*, 025005;
  b) C. H. Chen, V. M. B. Crisostomo, W. N. Li, L. Xu, S. L. Suib, *J. Am. Chem. Soc.* 2008, *130*, 14390–14391;
  c) R. D. K. Misra, D. Depan, J. Shah, *Phys. Chem. Chem. Phys.* 2013, *15*, 12988–12997;
  d) L. Raehm, A. Mehdi, C. Wickleder, C. Reye, R. J. P. Corriu, *J. Am. Chem. Soc.* 2007, *129*, 12636–12637;
  e) Y. Yamauchi, *J. Ceram. Soc. Jpn.* 2013, *121*, 831–840.
- [9] a) X. Z. Lin, Z. Y. Yuan, *Eur. J. Inorg. Chem.* 2012, 2661–2664; b) T. Kimura, K. Kato, Y. Yamauchi, *Chem. Commun.* 2009, 4938–4940; c) R. M. P. Colodrero, G. K. Angeli, M. B. Garcia, P. O. Pastor, D. Villemin, E. R. Losilla, E. Q. Martos, G. B. Hix, M. A. G. Aranda, K. D. Demadis, A. Cabeza, *Inorg. Chem.* 2013, *52*, 8770–8783; d) P. Xiao, *RSC Adv.* 2013, *3*, 5127–5130.
- [10] a) J. Morizzi, M. Hobday, C. Rix, J. Mater. Chem. 2001, 11, 794–798;
   b) S. S. Iremonger, J. Liang, R. Vaidhyanathan, I. Martens, G. K. H. Shimizu, T. D. Daff, M. Z. Aghaji, S. Yeganegi, T. K. Woo, J. Am. Chem. Soc. 2011, 133, 20048–20051.
- [11] a) G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* 2000, *12*, 1268–1272;
   b) M. Vasylyev, R. Neumann, *Chem. Mater.* 2006, *18*, 2781–2783.
- [12] a) M. Pramanik, A. Bhaumik, Chem. Eur. J. 2013, 19, 8507–8514; b) M.
   Pramanik, A. K. Patra, A. Bhaumik, Dalton Trans. 2013, 42, 5140–5149.
- [13] a) Y. Sui, X. Fang, R. Hu, Y. Xu, X. Zhou, X. Fu, *Mater. Lett.* 2007, *61*, 1354–1357; b) N. G. Armatas, W. Ouellette, K. Whitenack, J. Pelcher, H. Liu, E. Romaine, C. J. O'Connor, J. Zubieta, *Inorg. Chem.* 2009, *48*, 8897–8910; c) Y. Sui, X. Fu, J. Chen, L. Yin, *Catal. Commun.* 2008, *9*, 2616–2619; d) H. Tan, W. Chen, D. Liu, X. Feng, Y. Li, A. Yan, E. Wang, *Dalton Trans.* 2011, *40*, 8414–8418; e) J. D. Compain, P. Mialane, J. Marrot, F. Secheresse, W. Zhu, E. Oldfield, A. Dolbecq, *Chem. Eur. J.* 2010, *16*, 13741–13748.
- [14] a) C. Lv, R. N. N. Khan, J. Zhang, J. Hu, J. Hao, Y. Wei, *Chem. Eur. J.* 2013, *19*, 1174–1178; b) H. El Moll, A. Dolbecq, I. M. Mbomekalle, J. Marrot, P. Deniard, R. Dessapt, P. Mialane, *Inorg. Chem.* 2012, *51*, 2291–2302; c) S. Tanaka, M. Annakaab, K. Sakai, *Chem. Commun.* 2012, *48*, 1653–1655.
- [15] a) Y. H. Chuang, H. Liu, C. J. O'Connor, J. Zubieta, *Inorg. Chem. Commun.* 2008, 11, 1205–1208; b) K. P. Rao, V. Balraj, M. P. Minimol, K. Vidyasagar, *Inorg. Chem.* 2004, 43, 4610–4614.

- [16] a) M. J. Tebbe, W. A. Spitzer, F. Victor, S. C. Miller, C. C. Lee, T. R. Sattelberg, Sr., E. McKinney, J. C. Tang, J. Med. Chem. 1997, 40, 3937–3946;
  b) M. T. Migawa, J. L. Giradet, J. A. Walker, G. W. Koszalka, S. D. Chamberlain, J. C. Drach, L. B. Townsend, J. Med. Chem. 1998, 41, 1242–1251;
  c) M. J. Climent, A. Corma, S. Iborra, S. Martinez-Silvestre, ChemCatChem 2013, 5, 3866–3874.
- [17] M. Roth, M. L. Morningstar, P. L. Boyer, S. H. Hughes, R. W. Buckheit, Jr., C. J. Michejda, J. Med. Chem. 1997, 40, 4199–4207.
- [18] a) P. Lindberg, P. Nordberg, T. Alminger, J. Med. Chem. 1986, 29, 1327– 1329; b) K. J. Spivak, Z. Amit, Physiol. Behav. 1986, 36, 457–463; c) G. Navarrete-Vázquez, L. Yépez, A. H. Campos, Bioorg. Med. Chem. 2003, 11, 4615–4622.
- [19] a) R. N. Nadaf, S. A. Siddiqui, T. Daniel, R. J. Lahoti, K. V. Srinivasan, J. Mol. Catal. A 2004, 214, 155–160; b) V. A. Sontakke, S. Ghosh, P. P. Lawande, B. A. Chopade, V. S. Shinde, ISRN Org. Chem. 2013, 2013, 1–7; c) N. D. Kokare, J. N. Sangshetti, D. B. Shinde, Synthesis 2007, 18, 2829–2834.
- [20] a) A. P. Wight, M. E. Davis, *Chem. Rev.* 2002, *102*, 3589–3614; b) J. Weitkamp, M. Hunger, U. Rymsa, *Microporous Mesoporous Mater.* 2001, *48*, 255–270; c) M. Pramanik, A. Bhaumik, *J. Mater. Chem. A* 2013, *1*, 11210–11220.
- [21] Y. Zhou, M. Antonietti, J. Am. Chem. Soc. 2003, 125, 14960-14961.
- [22] J. Ovenstone, K. Yanagisawa, Chem. Mater. 1999, 11, 2770-2774.
- [23] R. Thiruvengadathan, V. Korampally, A. Ghosh, N. Chanda, K. Gangopadhyay, S. Gangopadhyay, *Rep. Prog. Phys.* 2013, *76*, 066501.
- [24] J. Zečević, C. J. Gommes, H. Friedrich, P. E. de Jongh, K. P. de Jong, Angew. Chem. Int. Ed. 2012, 51, 4213–4217; Angew. Chem. 2012, 124, 4289–4293.
- [25] a) M. Kruk, M. Jaroniec, Chem. Mater. 2001, 13, 3169–3183; b) A. Modak,
   J. Mondal, A. Bhaumik, ChemCatChem 2013, 5, 1749–1753.
- [26] a) G. Cao, R. C. Haushalter, K. G. Strohmaiert, *Inorg. Chem.* **1993**, *32*, 127–128; b) J. Li, G. Wang, Z. Shi, M. Yang, R. L. Luck, *Solid State Sci.* **2009**, *11*, 1955–1960.
- [27] Y. Yan, U. T. Bornscheuer, R. D. Schmid, *Biotechnol. Bioeng.* **2002**, *78*, 31 34.
- [28] F. H. Elbatal, A. M. Abdelghany, R. L. Elwan, J. Mol. Struct. 2011, 1000, 103–108.
- [29] S. M. Horner, S. Y. Tyree, Jr., Inorg. Chem. 1963, 2, 568-571.
- [30] K. Sarkar, T. Yokoi, T. Tatsumi, A. Bhaumik, Microporous Mesoporous Mater. 2008, 110, 405-412.
- [31] K. Antoniak, P. Kowalik, W. Prochniak, M. Konkol, A. Wach, P. Kustrowski, J. Ryczkowski, Appl. Catal. A 2012, 423, 114–120.
- [32] G. D. Khattak, M. A. Salim, A. S. Al-Harthi, D. J. Thompson, L. E. Wenger, J. Non-cryst. Solids 1997, 212, 180–191.
- [33] a) S. K. Das, M. K. Bhunia, A. K. Sinha, A. Bhaumik, ACS Catal. 2011, 1, 493–501; b) A. Sinhamahapatra, N. Sutradhar, B. Roy, P. Pal, H. C. Bajaj, A. B. Panda, Appl. Catal. B 2011, 103, 378–387; c) G. V. A. Martins, G. Berlier, C. Bisio, S. Coluccia, H. O. Pastore, L. Marchese, J. Phys. Chem. C 2008, 112, 7193–7200.
- [34] a) Y. Riadi, R. Mamouni, R. Azzalou, M. E. Haddad, S. Routier, G. Guillaumet, S. Lazar, *Tetrahedron Lett.* 2011, *52*, 3492–3495; b) P. Salehi, M. Dabiri, M. A. Zolfigol, S. Otokesh, M. Baghbanzadeh, *Tetrahedron Lett.* 2006, *47*, 2557–2560.
- [35] A. Dutta, J. Mandal, A. K. Patra, A. Bhaumik, Chem. Eur. J. 2012, 18, 13372-13378.
- [36] M. Khoshneviszadeh, N. Edraki, K. Javidnia, A. Alborzi, B. Pourabbas, J. Mardaneh, R. Miri, *Bioorg. Med. Chem.* 2009, 17, 1579–1586.
- [37] D. Kong, J. Zon, J. McBee, A. Clearfield, Inorg. Chem. 2006, 45, 977-986.

Received: May 2, 2014 Revised: May 27, 2014 Published online on August 14, 2014