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Periodic Mesoporous Organosilicas Consisting of 3D Hexagonally Ordered Interconnected Globular Pores

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A new family of periodic mesoporous organosilicas with 100% E-configured ethylene-bridges and controllable pore systems is presented. 2D hexagonally ordered hybrid nanocomposites consisting of cylindrical pores are obtained, of which some are filled with solid material. The architectural composition of these hybrid materials can be accurately controlled by fine-tuning the reaction conditions; that is, there is a unique correlation between the reaction mixture acidity and the amount of confined mesopores. This correlation is related to the filling of the pores with solid material whereby the length of the pore channels can be tailored. Hereby the mesophasic either shifts toward long-ranged 2D hexagonally ordered open cylinders or toward 3D hexagonally ordered interconnected spheres. The synthesis of these organic—inorganic hybrid composites is straightforward via the direct condensation of \( E-1,2\text{-bis(triethoxysilyl)} \) ethene, in the presence of pluronic P123. The true nature of these periodic mesoporous organosilicas is disclosed by means of nitrogen gas physisorption, nonlocal density functional theory, SAXS, TEM, and electron-tomography.

Introduction

Over the last few decades, organic—inorganic hybrid nanocomposites with well-defined supramolecular structures have attracted considerable attention due to their potential applications in various fields going from catalysis,\(^1\) adsorption,\(^2,3\) and environmental technology\(^4\) to nanoelectronics,\(^5\) sensing,\(^6\) and controlled drug release.\(^7\) These hybrid materials are synthesized either through postsynthetic grafting of organic entities onto the surface silanol groups, or through co-condensation of organosilanes, typically \( \text{R}’\text{Si(OR)}_3 \), with tetraethoxysilane. In 1999, several research groups reported on a new class of organic—inorganic hybrid composites which are developed through direct condensation of bridged organosilanes, commonly \((\text{RO})_3\text{Si} – \text{R}’\text{Si(OR)}_3\), in the presence of a surfactant template.\(^8,9\) Designated as PMOs (periodic mesoporous organosilicas), these hybrid composites are unique in their compositional structure. The organic groups are covalently bonded within the siliceous network and hence are an intrinsic constituent of the mesoporous framework. The high loading and uniform distribution of organic groups in the pore walls of these open porous structures is a distinctive feature which allows for the easy tailoring of both the chemical and physical properties while preserving the structural stability of the porous framework.

To date, much effort in research has been made into both the development of PMOs with novel organic bridging units and structures as into revealing the mechanism whereby such materials take shape.\(^10,11\) The pore structure and pore channel connectivity can be tailored by fine-tuning the reaction conditions, such as type of structure directing agent, acid concentration, presence of additives, reaction temperature, etc. In particular poly(alkylene oxide)-type block copolymers have proven to be versatile surfactants for the preparation of large pore ordered materials with various porous architectures.\(^12\) Their tuneable hydrophilic/hydrophobic volume ratio provide a certain degree of control in designing ordered mesoscopic materials with desirable structures.

Here we report on the controlled synthesis and detailed characterization of periodic mesoporous organosilicas with \( E \)-configured ethylene-bridges with the aid of pluronic P123 as a structure directing agent. The mesostructural composition of these materials can be easily and gradually engineered to consist either of 2D hexagonally packed cylindrical pores with typical \( \text{P6}_3\text{mm} \) symmetry or 3D hexagonally stacked interconnected globular pores with \( \text{P6}_3\text{mm} \) symmetry.

Experimental Section

General. Triblock copolymer \( \text{EO}_2\text{PO}_{34}\text{EO}_2 \) (pluronic P123), vinyltriethoxysilane, and \((\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CPh} \) (Grubbs’ first generation), were purchased from Aldrich. Vinyltriethoxysilane was distilled and degassed before use. \( E-1,2\text{-bis(Triethoxysilyl)}\) Ethene (BTSE) was synthesized as described earlier.\(^29\) To a Schlenk flask under argon, 0.0535 g of \((\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CPh} \) (0.065 mmol) and 42.95 mL of VTES (0.2038 mol) are added. The mixture is left to stir for one hour and subsequently refluxed for two hours. Unreacted VTES is distilled off, after which BTSE is vacuum distilled to give a clear colorless liquid.

Synthesis of Ethylene-Bridged PMOs. In a typical synthesis procedure of an \( E \)-configured ethylene-bridged PMO, 1.00 g of P123 is diluted in an acidified solution containing 34.10 mL of distilled \( \text{H}_2\text{O} \) and 0.456 mL of...
concentrated HCl. The solution is stirred for 1.5 h at room
temperature, upon which 1.90 mL of E-1,2-bis(triethoxysi-
lyl)ethene is added. This solution is stirred for 4 h at 35 °C and
successively aged for an additional 17 h at 90 °C. The surfactant
template is removed by Soxhlet extraction using acetone over
a period of 5 h. A series of PMOs synthesized with different
acid concentrations was prepared: 1.58, 1.00, 0.75, 0.492, 0.248,
0.158, 0.125, and 0.063 mol/L. All other reactions parameters
were kept constant. These samples are denoted as EBP-1 to
EBP-8, with EBP = ethenylene-bridged PMO. An additional
PMO sample was prepared using n-butanol as a cosolvent. This
sample was prepared using the procedure described above in a
HCl solution of 0.8 mol/L, in the presence of 2.4 mL of
n-butanol. This PMO is abbreviated as EBP-9.

**Characterization.** Nitrogen gas adsorption experiments were
conducted at 77 K using a BelSorp-mini II gas analyzer. Samples
were vacuum-dried overnight at 90 °C prior to analysis. The
core size distribution (PSD) was calculated from the desorption
branch using NLDF. The micropore volume, $V_{\text{mic}}$, was
calculated using the $t$-plot method. TEM and ET samples were
prepared by grinding the dry powder in a mortar, subsequently
dispersing a portion of the material in ethanol using ultrasoni-
cation for 60 s, after which a few droplets of the suspension
were placed on a Quantifoil R2/1 lacey carbon support film,
followed by drying under a lamp. Alternatively, ET samples
were prepared by applying the dry powder directly to the TEM
grid. The carbon support film for ET experiments had 5 or 10
nm gold colloids attached to it, which aid in the alignment of
the data set with respect to a common origin and rotation axis.
TEM images and ET image series were acquired in bright-field
tilt series using a Tecnai 20 electron microscope (FEI Company).
The microscope, operated at 200 keV, was equipped with a LaB$_6$
 electron source, a Twin objective lens, and a 2k CCD Camera (TVIPS, Gauting). Acquisition of single-axis tilt-series was performed in Xplore3D (FEI company) over an angular range of ±70° at 2° increments. Alignment, reconstruction, and denoising were carried out in IMOD. Reconstructions were denoised by nonlinear anisotropic diffusion. Segmentation was done in IMOD or Amira 3.1 (Mercury Computer Systems, Inc.).

Small-angle X-ray scattering (SAXS) experiments were carried out at the Dutch-Belgian Beamline (DUBBLE, BM26-B) of the European Synchrotron Radiation Facility (ESRF, Grenoble). Data were collected during 60 s using an X-ray wavelength, $\lambda$, of 0.775 Å on a two-dimensional position sensitive gas-filled wire chamber detector at 4 m from the sample. The covered scattering vector range 0.0027 < $q$ < 0.04 Å$^{-1}$ was calibrated with a Silver Behenate specimen ($s = 2 \sin \theta/\lambda$, where $2\theta$ is the scattering angle). The isotropic data were corrected for the detector response, azimuthally integrated, and normalized to the intensity of the primary beam, measured by an ionization chamber placed downstream from the sample. The background scattering due to the experimental setup and the sample holder was subtracted according to standard procedures, taking into account transmission differences. Hermetic aluminum DSC pans (TA instruments) were used as sample holders.

**Results and Discussion**

**N$_2$-Physisorption.** A set of diastereoisomerically pure E-
configured ethenylene-bridged PMOs (abbreviated as EBP) with
various pore systems was developed by fine-tuning the acidity
of the reaction mixture during the synthesis. Typical nitrogen
isotherms of these EBPs are illustrated in Figure 1. The
described PMOs are characterized by type IV adsorption
isotherms with sharp one-step capillary condensations, indicating
uniform mesopores. The desorption isotherms are distinctive
for each of these mesoporous systems. Herein, the occurrence
of open cylindrical, blocked, or confined interconnected pores
of different sizes and shapes determine the desorption behavior.
The capillary evaporation is related to the equilibrium gas—liquid
phase transition in the pores. In the case of EBP-9, a one-step
desorption isotherm and a narrow H1 type hysteresis loop is
apparent. These characteristics of equilibrium desorption are
typical for materials with cylindrical mesopores which are open
at both ends. EBP-1 on the other hand, reveals a delayed one-
step desorption isotherm and a H2 type hysteresis loop which
is typical for materials with confined mesopores or mesopores
with ink-bottle necks. When large mesopores are connected and
confined by smaller passages, the capillary evaporation of the
condensed nitrogen in the pore center is delayed until the vapor
pressure is reduced below the equilibrium desorption pressure
of these passages. This phenomenon is often referred to as pore
blocking. The relative pressure at which the hysteresis loop
closes is related to the size of the interconnecting passages, or
pore entrances in the case of ink-bottle pores, and on the number
of interconnecting passages versus mesopore cavities. However,
in the case of nitrogen physisorption at 77 K, the close point of
the hysteresis loop can never be smaller than a relative pressure
of ~0.42. Below this relative pressure value, the capillary
condensate is unstable, and spontaneous cavitation of nitrogen
occurs at $p/p_0 > 0.42$, resulting in a sharp capillary evaporation
step in the desorption isotherm. This is clearly illustrated by
EBP-1 in Figure 1.

EBP-6 and EBP-2, shown in Figure 1, exhibit remarkable
two-step desorption isotherms, indicating the presence of both
open cylindrical and confined or blocked mesopores. Herein,
the high relative pressure desorption step corresponds to the
equilibrium desorption in open mesopores. At these relatively

**TABLE 1: NLDF Data of Ethenylene-Bridged PMOs Synthesized at Different Acid Concentrations**

<table>
<thead>
<tr>
<th>sample</th>
<th>$-\log$ [HCl]</th>
<th>BP [%]</th>
<th>$V_{\text{mic}}$ [cm$^3$/g]</th>
<th>$D_p$ [nm]</th>
<th>pore diameter distribution&lt;sup&gt;d&lt;/sup&gt; [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBP-1</td>
<td>−0.200</td>
<td>83.3</td>
<td>0.15</td>
<td>6.8</td>
<td>8.3, 10.8, 67.4, 13.5</td>
</tr>
<tr>
<td>EBP-2</td>
<td>0</td>
<td>71.5</td>
<td>0.08</td>
<td>6.8</td>
<td>8.3, 1.0, 64.9, 25.8</td>
</tr>
<tr>
<td>EBP-3</td>
<td>0.125</td>
<td>65.8</td>
<td>0.05</td>
<td>7.0</td>
<td>3.6, 0, 63.4, 33.0</td>
</tr>
<tr>
<td>EBP-4</td>
<td>0.308</td>
<td>58.6</td>
<td>0.06</td>
<td>7.0</td>
<td>4.3, 0, 56.0, 39.7</td>
</tr>
<tr>
<td>EBP-5</td>
<td>0.606</td>
<td>41.5</td>
<td>0.10</td>
<td>7.0</td>
<td>9.9, 3.3, 36.0, 50.8</td>
</tr>
<tr>
<td>EBP-6</td>
<td>0.801</td>
<td>32.7</td>
<td>0.16</td>
<td>7.0</td>
<td>14.3, 6.2, 26.0, 53.5</td>
</tr>
<tr>
<td>EBP-7</td>
<td>0.903</td>
<td>19.3</td>
<td>0.15</td>
<td>7.2</td>
<td>12.6, 8.1, 15.3, 64.0</td>
</tr>
<tr>
<td>EBP-8</td>
<td>1.203</td>
<td>10.9</td>
<td>0.13</td>
<td>7.3</td>
<td>15.4, 8.3, 8.3, 68.0</td>
</tr>
<tr>
<td>EBP-9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.0</td>
<td>5.4</td>
<td>0.14</td>
<td>8.1</td>
<td>7.6, 13.1, 4.3, 75.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Blocked pores (calculated using NLDF).<sup>b</sup> Micropore volume (calculated using $t$-plot).<sup>c</sup> Pore diameter, calculated from the desorption isotherm using NLDF.<sup>d</sup> Calculated from the desorption isotherm using NLDF. Synthesized with n-butanol.29
high pressures, the blocked pores remain filled until the vapor relative pressure is reduced to $\sim 0.48$, at which the cavitation of the condensed nitrogen in the blocked pores takes place. That is, the fraction of blocked pores in EBP-2 is substantially larger than in EBP-6. These unusual two-step desorption isotherms are very similar to those previously reported upon by Van Der Voort et al.\textsuperscript{36} Herein, the mesopores of the described silica materials (PHTS or plugged hexagonal templated silicas) are blocked by microporous nanocapsules, referred to as plugs. However, the PMOs described in this study reveal a different morphology, as will be elucidated.

A remarkable feature of these PMOs is the dependence of the pore-blocking on the acidity of the reaction mixture. By adjusting the acidity, the fraction of open and blocked mesopores can be accurately fine-tuned, as illustrated in Figure 2. To the best of our knowledge, such a correlation has never been reported before. A detailed study of the isotherms was performed by means of an NLDFT analysis, which allows for the calculation of the mesopores size distributions and determination of volumes of open and blocked pores.\textsuperscript{37} The NLDFT data are given in Table 1.

When comparing EBP-1 to EBP-8, it is clear from the pore diameter distributions in Table 1 that the described PMOs exhibit both blocked and open mesopores. Herein, the contribution of blocked and open pores is calculated from the pore size distribution (PSD) function between 40 and 60 Å and above 60 Å, respectively. The corresponding PSD graphs are given in the Supporting Information, Figure SI-1. The desorption of nitrogen from the blocked pores occurs through the cavitation mechanism, thus the pore size distribution corresponding with the second step in the desorption branch is not related to the sizes of the blocked pores. The pore size distributions between 20 and 40 Å reflect the roughness of the pore walls.\textsuperscript{38} The micropores are calculated from the pore size distributions below 20 Å.

The absence of a correlation between the micropore volume and the relative fraction of blocked mesopores is a first indication that these PMO materials have different pore structures than PHTS. As the pore-blocking effect is related to the acidity of the reaction mixture, it seems to be a kinetic phenomenon. However, recently we reported the synthesis of well-ordered diastereoisomerically pure ethylene-bridged PMOs with open cylindrical mesopores under highly acidic conditions, with the aid of butanol as a cosolvent.\textsuperscript{29} By adapting this
synthesis procedure, no pore-blocking occurs at pH 0.1 (EBP-9) and nitrogen isotherms with a type H1 hysteresis are obtained (see Figure 1), whereas without butanol, about 66% of the mesopores are blocked. This suggests that the occurrence of pore-blocking, while being dependent on the pH of the reaction mixture, is not a purely kinetic happening.

To explain these findings and elucidate the structure of these PMO materials, a detailed study was carried out using SAXS, TEM and electron tomography (ET). Herein, three samples were investigated: (1) a PMO which consists of open cylindrical mesopores (EBP-9), (2) a PMO which consists of both open and blocked mesopores (EBP-6), and (3) a PMO which consists of blocked mesopores (EBP-1).

SAXS, TEM, and ET. Figure 3 gives both the SAXS pattern and the most probable underlying form factor curve of EBP-9. The SAXS pattern is typical for a well-ordered 2D hexagonal structure, revealing three well-resolved peaks which can be assigned to the (100), (110), and (200) reflections. The observed intensity can miss some expected reflections at s values where the form factor, in the present case due to the cylindrical lattice motif, goes through zero. After all, the observed scattered intensity is proportional to the product of the lattice interference function (producing the main reflections) with the form factor. This is helpful in determining the diameter of the cylinders. The missing (120) reflection and the equally intense (110) and (200) reflections lead to a cylinder with a diameter of 8.2 nm, which is in very good agreement with the pore size determined from the desorption isotherm using NLDFT, namely 8.1 nm. With a d_{100} spacing of 9.7 nm, EBP-9 has a unit cell of 11.2 nm.

The ordered structure of EBP-9 was confirmed by TEM, as illustrated in Figure 4. Both hexagonal and parallel patterns commonly associated with 2D hexagonal ordering are observed. TEM images reveal large ordered domains, up to hundreds of nanometers in size. To study the local three-dimensional pore structure of EBP-9, ET was employed. Figure 5 displays numerical cross-sections through reconstruction perpendicular and parallel to the pore direction. ET results show 2D hexagonally packed cylindrical pores with no significant pore blocking. A movie of consecutive cross-sections to illustrate the 3D structure more accurately can be found in the Supporting Information. The observed open pore channels are in good agreement with the N$_2$ physisorption measurements, although by ET in some cases pores that terminated inside the particle, which would lead to pore blocking, were observed too (see the Supporting Information, Figure SI-2). In addition it was found that a single particle can consist of multiple P6/mm domains with different pore directions.

The unit cell size was estimated to be about 10 nm, both by ET and TEM, which is smaller than the SAXS result. Similar observations were made previously on KIT-6 material. The difference in lattice spacing most likely arises from shrinking of the material upon exposure to the electron beam.

The experimental SAXS pattern and a suited, calculated cylinder form factor curve of EBP-6 are shown in Figure 6. Distinct reflections which can be assigned to a 2D hexagonal structure with a P6/mm space group are, (100), (200) and (120). The low intensity of the (110) reflection combined with the
comparable intensities of the (200) and (120) reflections, lead to a cylinder with a diameter of 7.0 nm, which is identical to the pore size calculated from the desorption isotherm using NLDFT. With a \( d_{100} \) spacing of 9.45 nm, EBP-6 has a unit cell of 10.9 nm. The overall diffraction pattern of EBP-6 is very similar to EBP-9, which can be associated with a well-ordered 2D hexagonal lattice of cylindrical pores. This is also in agreement with TEM results shown in Figure 7.

To resolve the local 3D pore structure of EBP-6 and to elucidate the nature of the pore-blocking, electron tomography was used. In the numerical cross-section of EBP-6 in Figure 8a, the 2D hexagonal ordering is clearly apparent. However, some pores are filled with solid material: that is, no pores are visible where they are supposed to be based on the 2D hexagonal lattice (Figure 8b). A movie of consecutive cross-sections to illustrate the 3D structure more accurately can be found in the Supporting Information. The sample consists of short pores that terminate inside the mesostructure and pores curved on a very local scale. These structural features rationalize the pore-blocking effect that is apparent from nitrogen physisorption. This leads us to the hypothesis that shorter pores are formed with increasing acidity.

The SAXS pattern and an appropriate theoretical form factor curve of EBP-1 are shown in Figure 9. The SAXS pattern is not characteristic for a 2D hexagonally ordered material but rather indicates, when considered in conjunction with the TEM data discussed below, a 3D hexagonal structure with a \( P6/mnm \) space group. When comparing the observed reflections with the expected theoretical reflections for a simple hexagonal packing of spheres, the two well-resolved peaks \( (s = 0.0104 \text{ and } 0.0189 \text{ Å}^{-1}) \) and the less-resolved peak \( (s = 0.0173 \text{ Å}^{-1}) \) can be assigned to the (100), (001), and (110) reflections of a 3D hexagonal lattice, respectively. Higher order reflections in the pattern are absent because of considerable lattice distortions (due to the presence of pores filled with material) and form factor effects. With a \( d_{100} \) spacing of 9.7 nm, EBP-1 has a unit cell \( a_0 = 11.2 \text{ nm} \). In the \( c \) direction, \( d_{001} = 5.25 \text{ nm} \).

The ordered structure of EBP-1 was confirmed by TEM, as illustrated in Figure 10. Herein, parallel, hexagonal, and square patterns are clearly visible, suggesting that the structure has a symmetry more complex than \( P6/mnm \). In context of the SAXS results, the TEM images taken from three different parts of the sample, are considered to reflect three different perspectives of a simple hexagonal lattice with \( P6/mnm \) symmetry, as illustrated in Figure 10.

A more detailed insight into the ordering of EBP-1 was obtained by electron tomography. ET results in Figure 11 indicate a 3D ordered structure consisting of globular pores. As illustrated in Figure 11a, it was often observed that voids were filled with solid material, similar as for EBP-6. However, a long-range order of the remaining voids is preserved (see the Supporting Information, Figure SI-3). In one instance globular pores and short pore channels were observed (see the Supporting Information, Figure SI-4). The local disorder, i.e., voids filled with solid material and changes in stacking (Figure 11c), complicates deriving a unit cell from neighboring voids. As to
how the globular pores are stacked in 3D, the SAXS data suggests a predominant $P6/mm$ symmetry with an AAA stacking of spheres. However, on the local scale, ET found a close-packed structure with an ABC stacking (see supporting movie).

When comparing the results obtained by SAXS, TEM, and ET with those obtained by nitrogen physisorption, the pore-blocking effect can be ascribed to the filling of the mesopores with solid material and to the shortening of the pore channels (pore confinement). For the PMOs with both open and blocked mesopores (EBP-2 to EBP-8), a fraction of the hexagonally packed cylinders terminate inside the mesostructure, thus forming short pore channels, as evidenced by ET. This phenomenon causes confinement of the adsorbed nitrogen. As only a fraction of the pores are blocked, the confinement of nitrogen is only partial and hence a two-step desorption isotherm is obtained. Consequently, the hysteresis of such a PMO is a combination of a H1 and a H2 type hysteresis. As the fraction of blocked pores versus open pores gradually increases with decreasing pH, the amount of confined nitrogen which desorbs at relatively low pressures increases, and the hysteresis gradually converts into a H2 type hysteresis. At very low pH values a 3D hexagonally ordered mesostructure consisting mainly of globular pores is found (EBP-1). These globular pores can be considered as confined cavities which are interconnected with each other by smaller passages (<4 nm). The H2 type hysteresis of EBP-1 is related to the absence of open cylindrical pores, to the confinement of the globular mesopores and to the filling of some of the mesopores with solid material, as evidenced by ET.

The effect of the synthesis pH on the pore structures of these PMOs is related to an alteration in the hydrophobic/hydrophilic volume ratio of the surfactant template. With increasing acidity of the reaction mixture, the ionization of the ethylene oxide chains of the triblock copolymer enhances the fraction of the hydrophilic block relative to the hydrophobic block, which causes an increase in the interfacial curvature of the mesophase. This can rationalize the formation of globular pores at very low pH values. By increasing the pH of the reaction mixture, the globular micelles coalesce into a 2D hexagonally ordered structure, leading to the formation of cylindrical pores. This phase transformation is illustrated in Figure 12.

When butanol is added to the reaction mixture, the generation of globular pores is circumvented and cylindrical pores are preferentially formed, even at very low pH values. Herein, butanol, which is most probably located mainly at the hydrophilic/hydrophobic interface of the surfactant micelles, stabilizes the cylindrical micellar aggregates and assists the conglomeration of the nano building units into a long-ranged 2D hexagonally packed mesoporous architecture. That is, butanol induces the transformation of the spherical surfactant-organosilica composite micelles into rodlike micelles. This sphere-to-rod transition can be explained by the dehydration of the ethylene oxide chains in the micelle corona, which is considered to be the driving force for this transition in nonionic surfactant systems.

**Conclusions**

A unique family of periodic mesoporous organosilicas with 100% $E$-configured ethylene-bridges consisting of both open and blocked mesopores is presented. By means of nitrogen gas physisorption, NLDFT, SAXS, TEM, and electron-tomography the detailed structures of these PMO materials were determined. The two-step nitrogen desorption isotherms were attributed to the generation of confined short pores and interconnected spherical pores. By varying the pH of the reaction mixture, the amount of confined pores could be accurately controlled. At very low pH values, 3D hexagonally ordered mesostructures consisting of globular pores are predominant. By increasing the pH, this mesophase converts to 2D hexagonally ordered...
structures consisting of cylindrical pores. When butanol is added to the reaction mixture, the generation of globular pores is circumvented and cylindrical pores are preferentially formed.

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**Supporting Information Available:** NLDFT pore size distributions; ET data of EBP-9 and EBP-1; ET movies of EBP-9, EBP-6, and EBP-1. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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