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# Three-Dimensional Triptycene-Based Covalent Organic Frameworks with *ceq* or *acs* Topology

Hui Li,<sup>§,†</sup> Fengqian Chen,<sup>§,†</sup> Xinyu Guan,<sup>†</sup> Jiali Li, Cuiyan Li, Bin Tang,<sup>\*,‡</sup> Valentin Valtchev,<sup>⊥,||</sup> Yushan Yan,<sup>#</sup> Shilun Qiu,<sup>†</sup> and Qianrong Fang<sup>\*,†</sup>

<sup>†</sup>State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, P. R. China

<sup>‡</sup>Deakin University, Institute for Frontier Materials, Geelong, Victoria 3216, Australia

<sup>⊥</sup>Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Laoshan District, Qingdao, Shandong 266101, P. R. China

<sup>||</sup>Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 6 Marechal Juin, 14050 Caen, France

<sup>#</sup>Department of Chemical and Biomolecular Engineering, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA

Supporting Information Placeholder

**ABSTRACT:** The growth of three-dimensional covalent organic frameworks (3D COFs) with new topologies has still been considered a great challenge due to limited high-connectivity building units. Here we report the design and synthesis of novel 3D triptycene-based COFs, termed JUC-568 and JUC-569, in the light of the deliberate symmetry-guided design principle. By combining a triangular prism (6-connected) node with a planar triangle (3-connected) or another triangular prism node, the targeted COFs adopt unreported *ceq* or non-interpenetrated *acs* topology, respectively. Both materials also show permanent porosity and impressive performance in the adsorption of CO<sub>2</sub> (~ 98 cm<sup>3</sup>/g at 273 K and 1 bar) and CH<sub>4</sub> (~ 48 cm<sup>3</sup>/g at 273 K and 1 bar), and especially in H<sub>2</sub> storage (up to 274 cm<sup>3</sup>/g or 2.45 wt% at 77 K and 1 bar), which is highest among all porous organic materials reported to date. Thus, this research provides a promising strategy for diversifying 3D COFs based on complicated building blocks and promotes their potential applications in energy storage and environment-related fields.

Covalent organic frameworks (COFs), an emerging family of crystalline porous polymers, are assembled from organic reactants by reversible covalent bonds.<sup>1-5</sup> Due to high surface areas, modular natures, and good thermal/chemical stabilities, COF materials have attracted considerable attention in gas storage/separation,<sup>6-9</sup> organic electronics,<sup>10-14</sup> heterogeneous catalysis,<sup>15-20</sup> and some other fields.<sup>21-25</sup> Over the past decade, most the reports were focused on conjugated two-dimensional (2D) sheets, in which the abundant building blocks allowed to establish well developed synthetic strategies.<sup>5</sup> By contrast, three-dimensional (3D) COFs are still less studied due to the scant availability of appropriate molecular building units and relatively complex structure determination.<sup>4</sup> Up till now, only very limited topologies in 3D COFs have been reported,<sup>26-34</sup> such as *dia*, *ctn*, and *bor*. Moreover, almost all know 3D COFs were constructed by using tetrahedral (4-connected) building blocks, including the derivatives of tetraphenylmethane, tetraphenylsilane, and adamantane, which

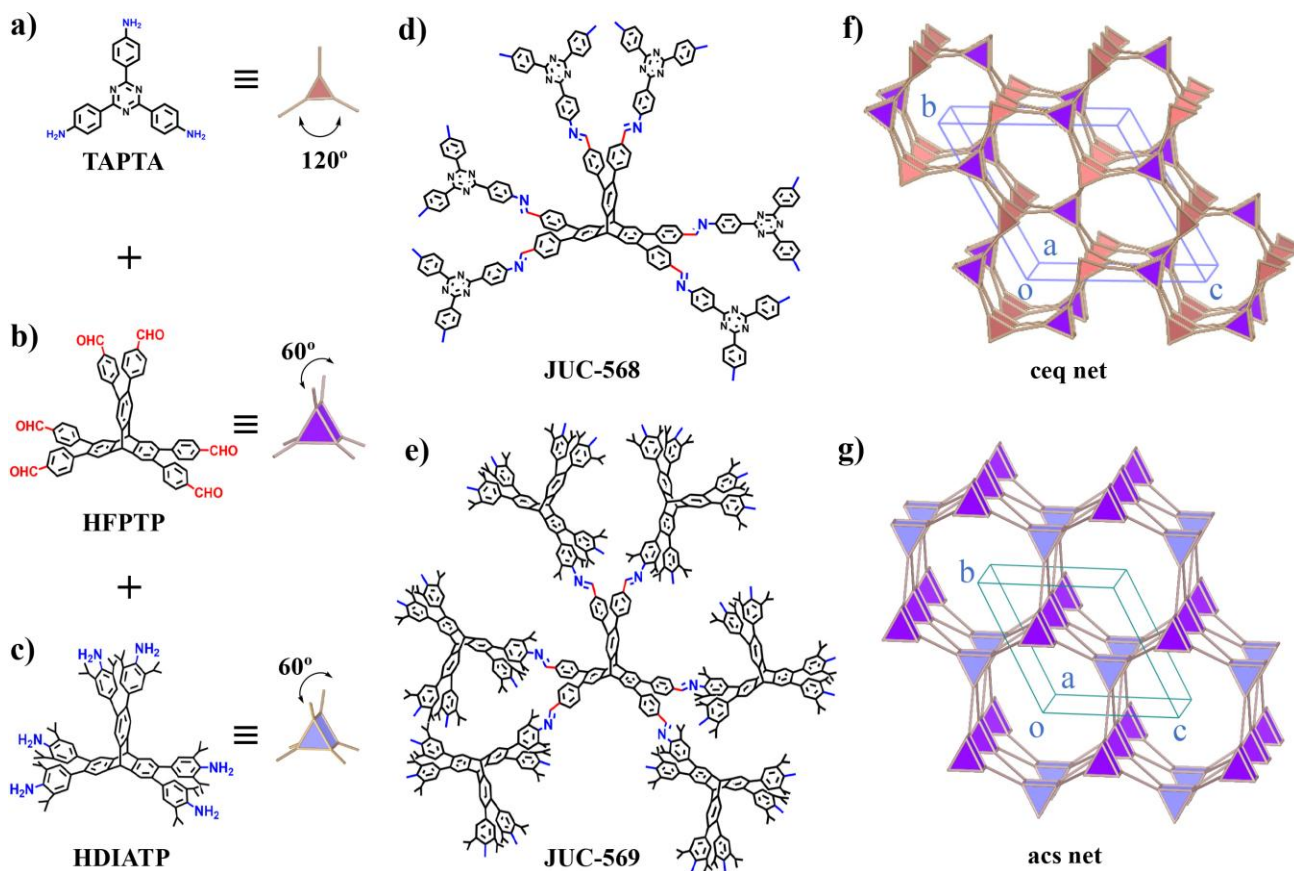
has greatly confined the structural diversities and functionalization of 3D COFs.

Despite the above issues, 3D COFs are considered a remarkable platform for practical applications due to their unique features,<sup>4</sup> e.g., inter-connective porous structures, high specific surface areas, and easily accessible active sites. In principle, the employment of high-connectivity building units, such as triangular prism (6-connected) monomers, can set up new architectures in 3D COFs, proved by several cases that appeared recently. For example, we synthesized the first 3D large-pore COF, JUC-564, with *stp* topology constructed from a triptycene-based triangular prism monomer, which has the largest pore (43 Å) among 3D COFs and record-breaking low density (0.108 g cm<sup>-3</sup>) in porous crystalline materials to date.<sup>35</sup> Subsequently, Cooper and co-workers also reported the first cage-based 3D COF, 3D-CageCOF-1, which is fabricated by an organic cage molecule as a triangular prism node and adopts a 2-fold interpenetrated *acs* topology.<sup>36</sup> It must be noted, however, that except for a few successful examples, 3D COFs based on high-connectivity monomers remain largely unexplored.

Herein we report the design and synthesis of new 3D COFs, termed JUC-568 and JUC-569 (JUC = Jilin University China), based on triptycene derivatives with a triangular prism node. By combining the triptycene-based monomer with a planar triangle (3-connected) node, JUC-568 shows a *ceq* topology. Besides, from the assembly of two similar triangular prism building units, JUC-569 adopts a non-interpenetrated *acs* topology. To the best of our knowledge, this study represents the first example of COFs with *ceq* or non-interpenetrated *acs* topology, which effectively promotes the structural varieties of 3D COFs. More importantly, owing to the high crystallinity and permanent porosity, these triptycene-based COFs demonstrate an impressive performance in the capture of CO<sub>2</sub> (~ 98 cm<sup>3</sup>/g at 273 K and 1 bar) and CH<sub>4</sub> (~ 48 cm<sup>3</sup>/g at 273 K and 1 bar), and particularly in H<sub>2</sub> adsorption (up to 274 cm<sup>3</sup>/g at 77 K and 1 bar), which is higher than those from all porous organic materials reported so far.

Our strategy for preparing 3D COFs with new topologies is based on the considered symmetry-guided design principle. A triptycene derivative, 2,3,6,7,14,15-hexa(4'-formylphenyl)

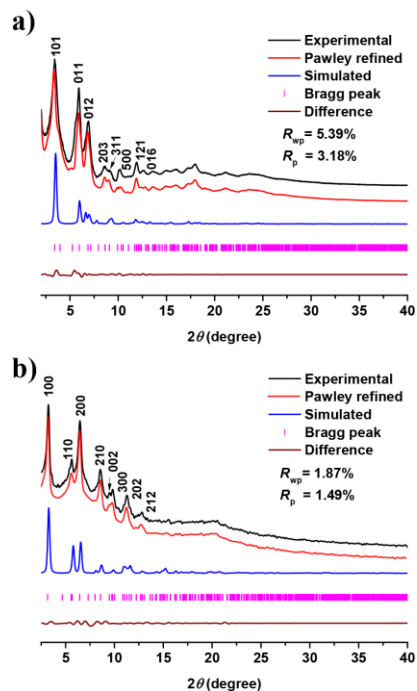
**Scheme 1. Schematic representation of the strategy for preparing 3D triptycene-based COFs<sup>a</sup>**



<sup>a</sup>Molecular structures of TAPTA (a) as a planar triangle (3-connected) node as well as HFPTP (b) and HDIATP (c) as triangular prism nodes (6-connected) building units. Two 3D triptycene-based COFs, denoted as JUC-568 (d) and JUC-569 (e), are constructed by the condensation reaction of HFPTP and TAPTA or HDIATP. An expanded [6 + 3] connected network (**ceq** topology) in JUC-568 (f), and an expanded [6 + 6] connected network (**acs** topology) in JUC-569 (g).

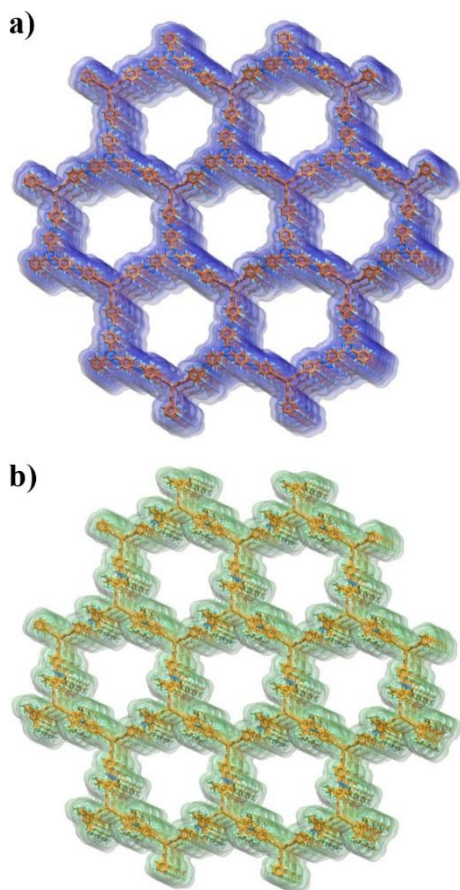
triptycene (HFPTP, Figure 1b), can perfectly act as a highly symmetrical triangular prism node. After analyzing the Reticular Chemistry Structure Resource (RCSR) database,<sup>37</sup> we found that only one possible topology (**acs**) is available for such a 6-connected nod. At the same time, there are multiple feasible topologies for the combination of 6-connected and 3-connected build units, such as **ceq**, **sab** and **dag**. Therefore, the condensation of HFPTP and a planar triangle (3-connected) monomer, 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPTA, Figure 1a), leads to an expanded [6 + 3] connected network (JUC-568, Figure 1d). Considering their link angles (60° for HFPTP and 120° for TAPTA), the targeted material is more likely to form the **ceq** topology (Figure 1f). Furthermore, to construct a pure 6-connected framework, another triangular prism monomer, 2,3,6,7,14,15-hexa(3',5'-diisopropyl-4'-amino) triptycene (HDIATP, Figure 1c) was also designed. JUC-569 (Figure 1e) can be obtained from the combination of two triangular prism monomers, HFPTP and HDIATP, with the same 6-connected node and link angle of 120°, which tends to a non-interpenetrated **acs** topology (Figure 1g).

The synthesis of JUC-568 was carried out by the solvothermal reaction of HFPTP (22.0 mg, 0.025 mmol) and TAPTA (17.7 mg, 0.05 mmol) in a mixture of dioxane, mesitylene, and acetic acid, with heating at 120 °C for 3 days; while JUC-569 was obtained by suspending HFPTP (22.0 mg, 0.025 mmol) and HDIATP (32.3 mg, 0.025 mmol) in a mixture of *o*-dichlorobenzene, *n*-butanol



**Figure 1.** PXRD patterns of JUC-568 (a) and JUC-569 (b).

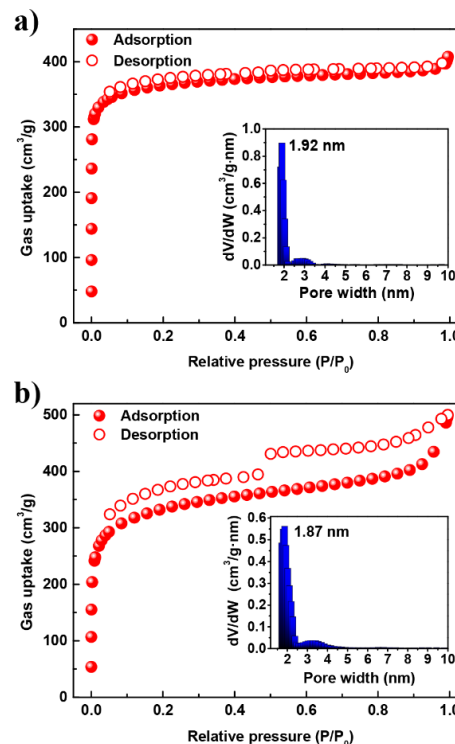
and acetic acid under 120 °C for 3 days. The as-synthesized COFs were insoluble in water or common organic solvents, such as hexane, acetone, *N,N*-dimethylformamide, ethanol, and tetrahydrofuran. The morphologies of both COFs were characterized by scanning electron microscopy (SEM), which show isometric crystals with an average size of 0.2  $\mu\text{m}$  (Figures S1 and S2). New COFs fourier transform infrared (FT-IR) spectra displayed peaks at 1598  $\text{cm}^{-1}$  for JUC-568 and 1625  $\text{cm}^{-1}$  for JUC-569, which are characteristic of C=N bond. At the same time, the depletion of peaks ascribed to C=O stretching vibration (1699  $\text{cm}^{-1}$  for HFPTP) and N-H stretching vibration ( $\sim 3323$   $\text{cm}^{-1}$  for TAPTA and  $\sim 3403$   $\text{cm}^{-1}$  for HDIATP) confirmed that aldehyde and amine groups had been transformed (Figures S3 and S4). Solid-state  $^{13}\text{C}$  cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy indicated that the presence of carbons from imine groups by the peaks at 158 ppm for JUC-568 and 162 ppm for JUC-569 (Figures S5 and S6). Thermogravimetric analysis (TGA) showed that both COFs had high thermal stability ( $\sim 450$  °C, Figures S7 and S8).



**Figure 2.** Extended structures of JUC-568 (a) and JUC-569 (b) viewed along *c*-axis.

The crystalline structures of 3D triptycene-based COFs were verified by the powder X-ray diffraction (PXRD) in conjunction with structural simulations (Figure 1). After a geometrical energy minimization by the Materials Studio software package,<sup>38</sup> the unit cell parameters were acquired with  $a = 49.570$  Å,  $b = 50.541$  Å,  $c = 15.618$  Å and  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  for JUC-568 based on a **ceq** net, while the unit cell parameters of JUC-569 with a non-interpenetrated **acs** net were  $a = b = 31.110$  Å,  $c = 18.468$  Å and  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . Moreover, the experimental PXRD patterns were accomplished by full profile pattern matching (Pawley)

refinement. Peaks at 3.43, 5.92, 6.82, 8.65, 9.08, 10.21, 11.86 and 12.70° for JUC-568 belong to the (101), (011), (012), (203), (311), (500), (121) and (016) Bragg peaks of the space group *Pm* (No. 6), and peaks at 3.24, 5.61, 6.47, 8.55, 9.48, 9.87, 11.30 and 12.84° for JUC-569 correspond to the (100), (110), (200), (210), (002), (300), (202) and (212) Bragg peaks of the space group *P-6* (No. 174). The calculated results can well match with those experimental ones with good agreement factors ( $R_p = 3.18\%$  and  $\omega R_p = 5.39\%$  for JUC-568;  $R_p = 1.49\%$  and  $\omega R_p = 1.87\%$  for JUC-569). In addition, we also tried alternative structures with different topologies, such as **sab** and **dag** net for JUC-568; however, there was a significant difference between the experimental and simulated PXRDs (Figures S9-11). In consideration of all these results, the obtained COFs were proposed to have the expected networks, **ceq** topology for JUC-568, and **acs** topology for JUC-569. Therefore, both COF materials show microporous cavities with  $\sim 1.98$  nm for JUC-568 and  $\sim 1.94$  nm for JUC-569 viewed along the *c*-axis (Figure 2).



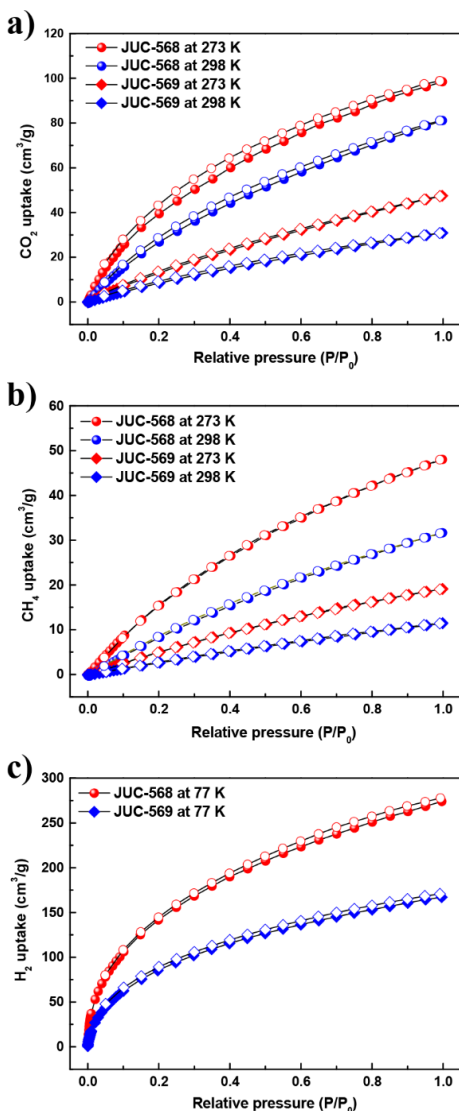
**Figure 3.**  $\text{N}_2$  adsorption-desorption isotherms for JUC-568 (a) and JUC-569 (b) at 77 K. Inserts: corresponding calculated pore-size distribution.

$\text{N}_2$  adsorption measurements determined the permanent porosity and specific surface areas of 3D triptycene-based COFs at 77 K. As can be seen in Figure 3, both COFs showed a sharp increase at low pressure (below 0.1  $P/P_0$ ), which reveals their microporous nature. The presence of textural mesopores in JUC-569 led to the isotherm inclination in the 0.8-1.0  $P/P_0$  range. Slight desorption hysteresis was observed, which is a consequence of the agglomeration of COF crystals.<sup>39</sup> The Brunauer–Emmett–Teller (BET) specific surface areas were 1433  $\text{m}^2/\text{g}$  for JUC-568 and 1254  $\text{m}^2/\text{g}$  for JUC-569, respectively (Figures S9-12). The non-local density functional theory (NLDFT) was used to calculate the pore-size distribution, and both COFs showed microporous cavities with  $\sim 1.92$  nm for JUC-568 and  $\sim 1.87$  nm for JUC-569 (inserts in Figure 3), which are in good agreement with the pore sizes pre-



dicted from their crystal structures ( $\sim 1.98$  nm for JUC-568 and  $\sim 1.94$  nm for JUC-569).

Furthermore, the uptakes of  $H_2$ ,  $CH_4$  and  $CO_2$  under one atmosphere were studied to expand the potential of 3D triptycene-based COFs in the greenhouse gas capture and energy storage. As shown in Figure 4, JUC-568 had higher adsorption capacity of  $CO_2$  ( $98\text{ cm}^3/\text{g}$  at 273 K and  $81\text{ cm}^3/\text{g}$  at 298 K),  $CH_4$  ( $48\text{ cm}^3/\text{g}$  at 273 K and  $32\text{ cm}^3/\text{g}$  at 298 K), and  $H_2$  ( $274\text{ cm}^3/\text{g}$  at 77 K) than JUC-569 ( $CO_2$ :  $47\text{ cm}^3/\text{g}$  at 273 K and  $31\text{ cm}^3/\text{g}$  at 298 K,  $CH_4$ :  $19\text{ cm}^3/\text{g}$  at 273 K and  $11\text{ cm}^3/\text{g}$  at 298 K, and  $H_2$ :  $167\text{ cm}^3/\text{g}$  at 77 K). Remarkably, the  $H_2$  storage capacity ( $274\text{ cm}^3/\text{g}$  or 2.45 wt%) of JUC-568 at 1 bar and 77 K is superior to those of porous organic materials (POMs) reported to date (Table S1), such as PPN-3 (1.58 wt%),<sup>40</sup> PAF-1 (1.66 wt%),<sup>41</sup> SPT-CMP1 (1.72 wt%),<sup>42</sup> and DL-COF-1 (2.09 wt%),<sup>43</sup> which can be attributed to the unique shape of triptycene as a rigid, fused-ring skeleton and three-fold symmetry building unit.<sup>44</sup>



**Figure 4.** The uptakes of  $CO_2$  (a),  $CH_4$  (b), and  $H_2$  (c) for JUC-568 and JUC-569 measured at different temperatures.

In summary, we have developed two 3D triptycene-based COFs, JUC-568 and JUC-569, with unreported **ceq** or non-interpenetrated **acs** topology, respectively. Noteworthy, JUC-568

possesses the permanent porosity and impressive performance in the uptakes of  $CO_2$  ( $98\text{ cm}^3/\text{g}$  at 273 K and 1 bar) and  $CH_4$  ( $48\text{ cm}^3/\text{g}$  at 273 K and 1 bar), and more importantly in  $H_2$  storage ( $274\text{ cm}^3/\text{g}$  or 2.45 wt% at 77 K and 1 bar), which is highest among porous organic materials reported so far. Thus, this work offers a prospective strategy for constructing 3D COFs from high-connectivity building blocks and facilitates their future applications in energy storage and environment protection.

### Supporting Information

Methods and synthetic procedures, SEM, FTIR, solid state  $^{13}C$  NMR, TGA, BET plot, and unit cell parameters. This material is available free of charge via the internet at <http://pubs.acs.org>.

### AUTHOR INFORMATION

#### Corresponding Author

\*qrfang@jlu.edu.cn or bin.tang@deakin.edu.au

#### Author Contributions

§H.L. and F.C. contributed equally to this work.

#### Notes

The authors declare no competing financial interests.

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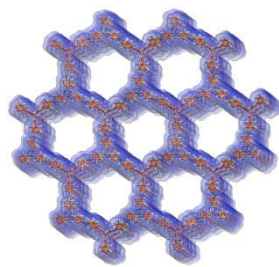
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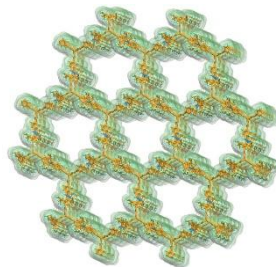
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