Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

On-surface synthesis of ethers through dehydrative coupling of hydroxymethyl substituents

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Contents

1. Additional results

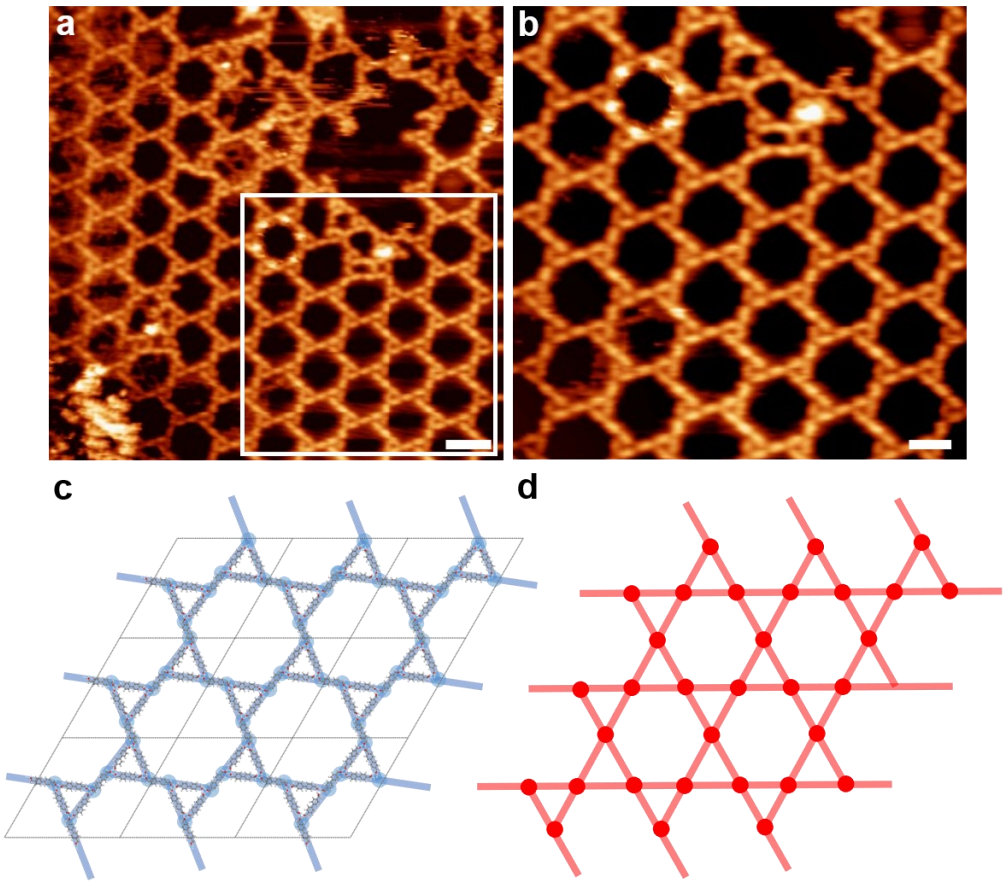

Figure S1. Kagome-like self-assembled pattern of molecule 1. (a) Large-scale and (b) close-up STM images showing the formation of the network structure after deposition of molecules **1** on Ag(111) held at RT. (b) is the zoomed area highlighted by a white box in (a). (c) Corresponding DFT model illustrating the self-assembled Kagome-like pattern and (d) Schematic diagram of Kagome lattice. (a) and (b) are acquired with V_t = - 1.8 V, I_t = 20 pA. Scale bars: (a), 3 nm; (b), 2 nm.

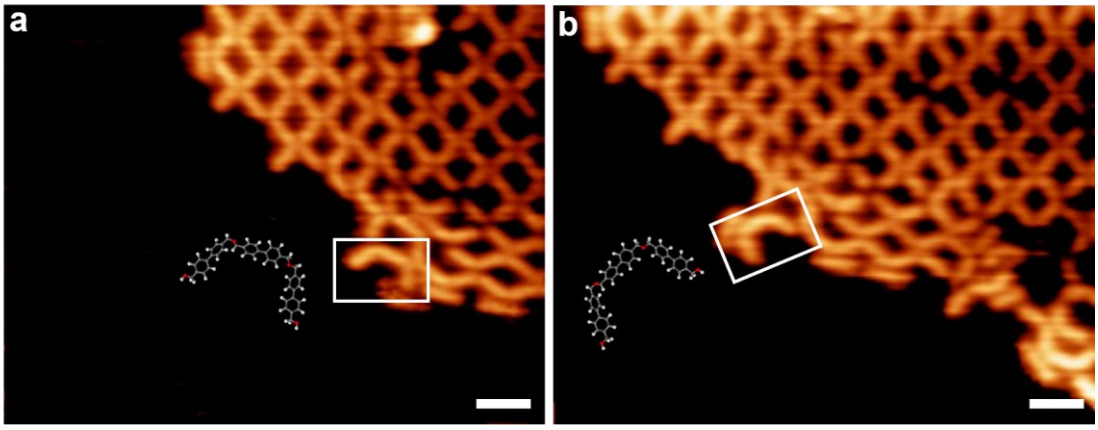

Figure S2. STM manipulation on an oligomeric ether. STM images (a) before and (b) after a lateral STM tip manipulation of a trimer structure highlighted by a rectangle, which provides strong evidence for the covalent nature of the oligomer. The corresponding structural models of the oligomer are shown beside the STM topographies of the oligomer. STM manipulation parameters: V_t = - 10 mV, I_t = 3.5 nA. (a) and (b) are acquired with V_t = - 1.0 V, I_t = 50 pA. All scale bars: 2 nm.

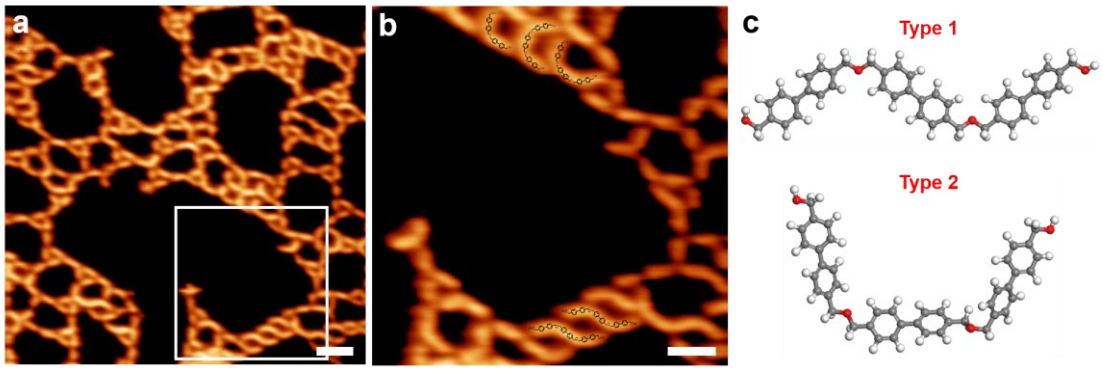

Figure S3. Two types of trimerized oligomers. (a) Large-scale and (b) close-up STM images showing two types of C-O-C bonded trimer structures with different configurations. The corresponding chemical schemes of the trimer structures are overlapped on some molecules in (b) for a better illustration. The region where (b) was imaged is indicated by the square in (a). (c) DFT optimized models of the two trimer structures. (a) and (b) are acquired with V = - 1.0 V, I = 100 pA. Scale bars: (a), 3 nm, (b), 2 nm.

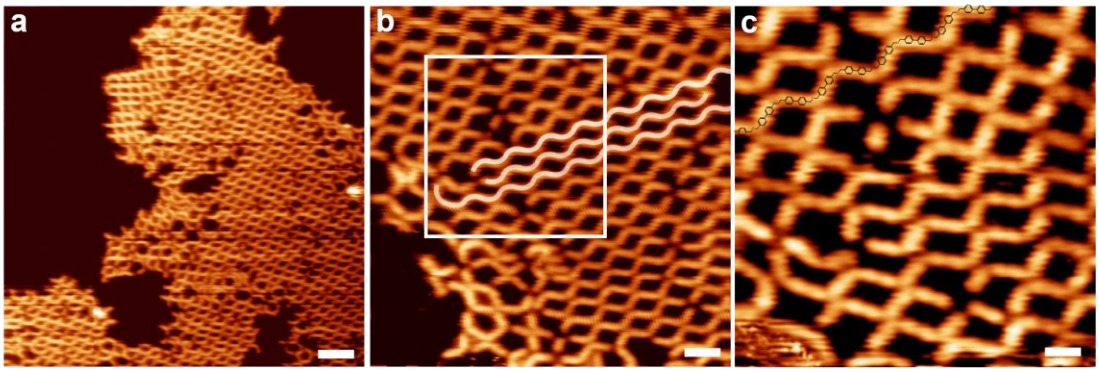

Figure S4. Additional STM images of the ether products on Ag(111) surface. (a) Overview and (b,c) zoom-in STM images showing the formation of one-dimensional ethers **2** with periodic C-O-C junctions on the surface. Some of ethers could extend a few tens of nanometers. The region where (c) was imaged is indicated by the square in (b). (a) and (b) are acquired with V_t = - 1.2 V, I_t = 50 pA. (c) is acquired with V_t = - 0.1 V, I_t = 100 pA. Scale bars: (a), 5 nm, (b), 2 nm, (c), 1 nm.

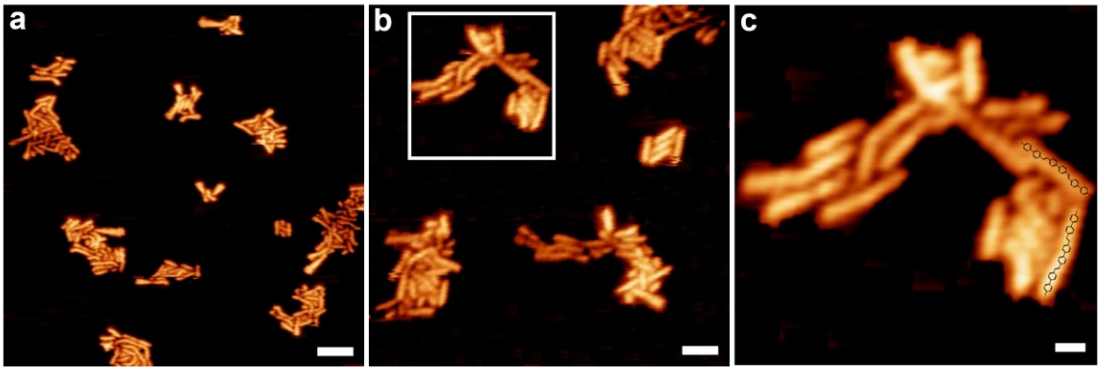

Figure S5. Additional STM images of product 3 on Ag(111) surface. (a) Overview (a) and zoom-in (b,c) STM images showing the formation of C-C coupled nanowires **3** on the surface. The region where (c) was imaged is indicated by the square in (b). (a), (b) and (c) are acquired with V_t = -1.0 V, I_t = 100 pA. Scale bars: (a), 5 nm, (b), 3 nm, (c), 1 nm.

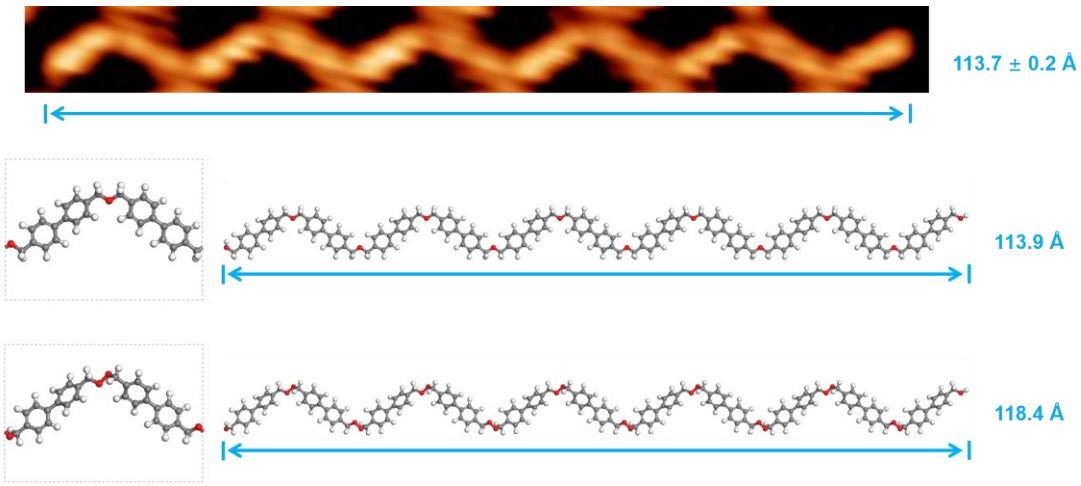

Figure S6. Confirmation of the C-O-C ether group. STM image of an zigzag undecamer. We have constructed and optimized the chain structures comprising the C-O-C (in the middle) and C-O-O-C (in the bottom) junctions, respectively. Their corresponding repeating units are shown on the left. The experimentally determined length of the undecamer is found to only agree with the C-O-C bonded ether chain.

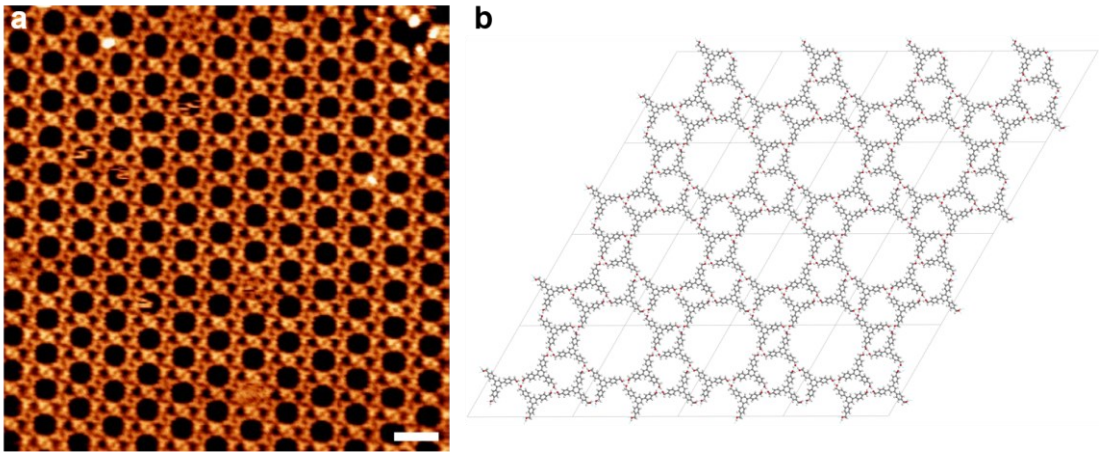

Figure S7. STM image of the self-assembled pattern of 4 on Ag(111) surface. (a) Large-scale STM image and (b) the corresponding DFT optimized model structure show the formation of a hexagonal porous pattern. The unit cell is indicated by lines in (b). (a) is acquired with V = - 1.2 V, I = 100 pA. Scale bars: (a), 5 nm.

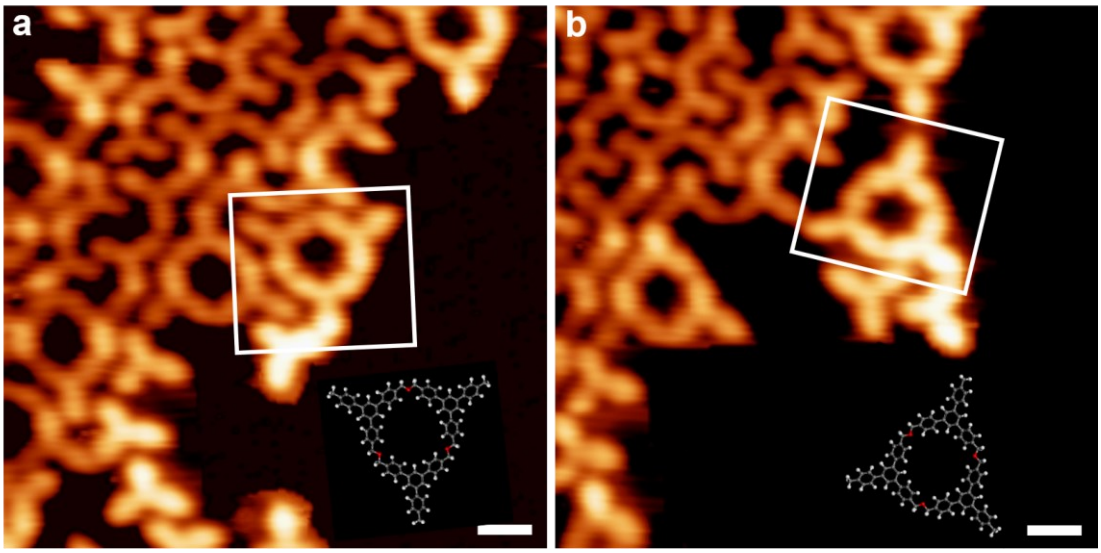

Figure S8. STM manipulation on an ether ring structure 5. STM images (a) before and (b) after a lateral tip manipulation of an ether ring which is highlighted by a white square, providing strong evidence for the covalent nature of the ring structure. The corresponding structural models of the ring structure are shown beside its STM topographies. STM manipulation parameters: V_t = -10 mV, I_t = 3.5 nA. (a) and (b) are acquired with V = -0.5 V, I = 100 pA. All scale bars: 1 nm.

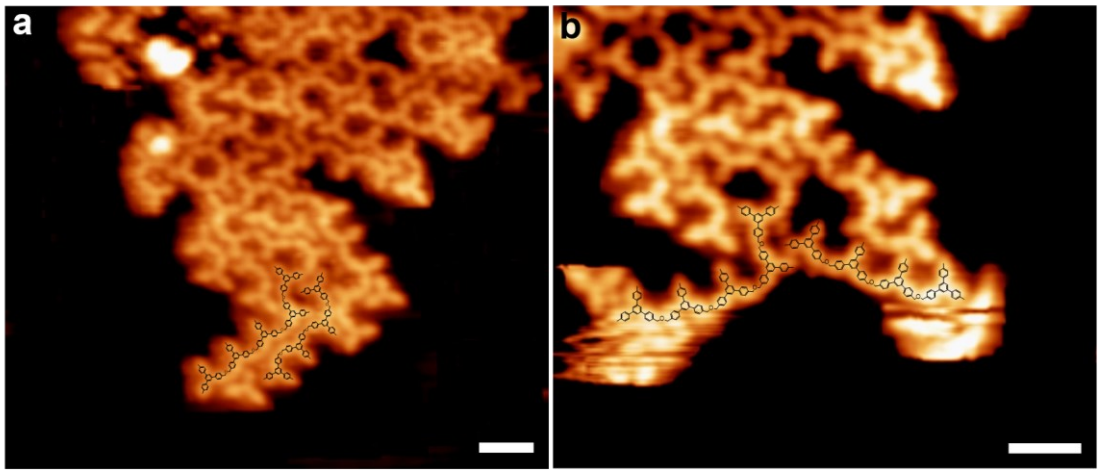

Figure S9. STM manipulation on the oligomeric chain structure formed by 5. STM images (a) before and (b) after a lateral tip manipulation of an ether chain, of which the chemical structures are overlaid on the STM images. STM manipulation parameters: V_t = -10 mV, I_t = 5.0 nA. (a) and (b) are acquired with V_t = - 0.5 V, I_t = 100 pA. All scale bars: 2 nm.

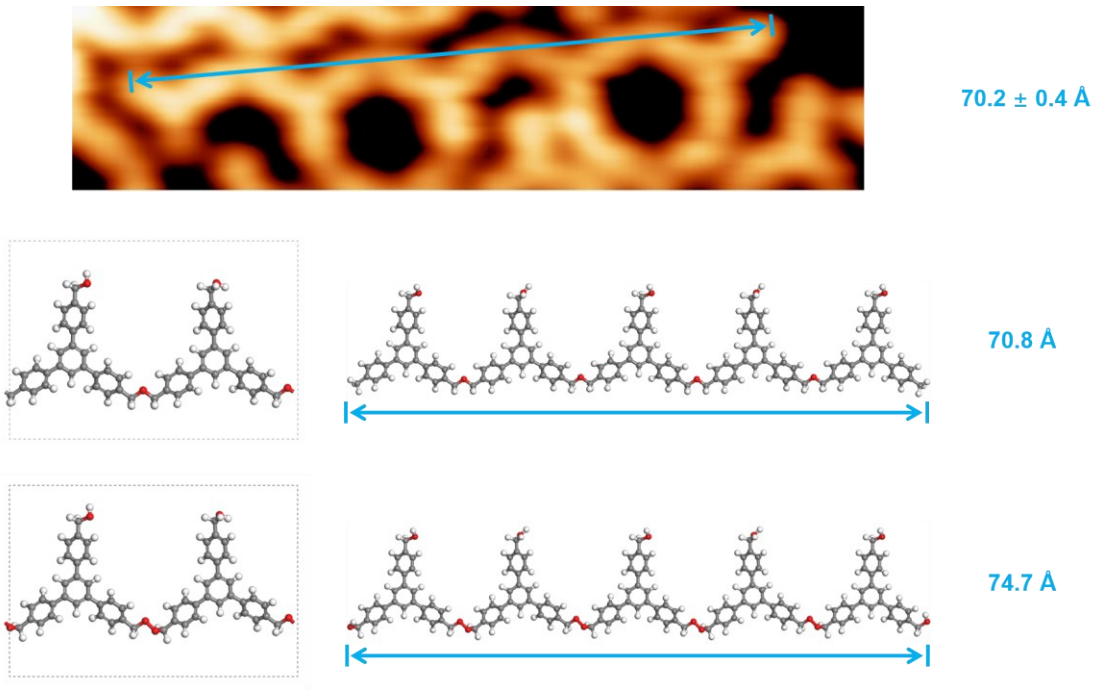

Figure S10. Confirmation of the C-O-C ether group in Fig. 3e. STM image of a pentamer formed by **4**. We have constructed and optimized the chain structures comprising the C-O-C (in the middle) and C-O-O-C (in the bottom) junctions, respectively. Their corresponding repeating units are shown on the left. The experimentally determined length of the undecamer only coincides with the C-O-C bonded ether chain.

2. Materials and Methods

STM characterization and sample preparation.

STM experiments were performed in a UHV system (base pressure 5 × 10^{-11} mbar) equipped with the low-temperature STM (Bosezi (Beijing) Co. Ltd. and Nanonis electronics), a molecular evaporator and other standard facilities for sample preparations. The metal substrates were prepared by several cycles of 1.5 keV Ar^+ sputtering followed by annealing at temperatures of around 800 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. After the molecular evaporator was thoroughly degassed, the **1** and **4** molecules were sublimated from the molecular evaporator at 373K and 418K, respectively. The sample was thereafter transferred within the UHV chamber to the microscope, We used a resistive heating filament to anneal the samples. Temperatures to trigger reactions were controlled by a DC power supply and monitored by an infrared thermometer. All STM measurements were acquired at liquid nitrogen temperature (~78 K), and thermal treatments to trigger chemical

reactions were conducted for 30 minutes if not stated otherwise. The STM images were analyzed using WsXM.[1]

Computational details.

The density functional theory (DFT) calculations are performed with the Vienna Ab Initio Simulation Package (VASP). Projector-augmented-wave pseudopotentials and the Perdew–Burke–Ernzerhof exchange-correlation functional were employed.[2,3] Van der Waals (vdW) interactions were taken into account using the dispersion corrected DFT-D3 method of Grimme.[4] All the structures were relaxed in DFT until residual forces on all unconstrained atoms were less than 0.03 eV/Å for geometry optimizations.

Charge density difference maps were computed by substracting the charge densities of individual molecules from the total system $\Delta\rho = \rho_{sys} - \rho_A - \rho_B - \rho_C$.

We used the climb image nudged elastic band (CI-NEB) method to find the saddle point along energy paths between the reactants and products.[5] The VASP transition state tools (VTST) was linked to the VASP package to allow for the CI-NEB method which has been proven to outperform the original NEB method implemented in VASP. We used the force-based Quick-Min optimizer to locate the saddle points.[6] The reaction pathway optimization was stopped until the forces acting on the images along the path were converged to be less than 0.05 eV/Å. All the computations were carried out using the high-performance cluster at Shanghai University.

3. References

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5. Henkelman, G., Uberuaga, B.P. & Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **113**, 9901-9904 (2000).
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