Electronic Supplementary Material (ESI) for ChemComm.


# Supplementary Information

# Structural transition and chemical reactivity of atomic carbon chains

*Siyuan Fang,*[a] *Xiao Tong,*[b] *Dario Stacchiola,*[b] *Yun Hang Hu*[a]*

a. Department of Materials Science and Engineering, Michigan Technological University, Houghton, Michigan 49931, United States.

b. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States.

*E-mail: yunhangh@mtu.edu

## Experimental Section

***Synthesis of sp-hybridized carbon chains:*** A mixture consisting of 0.064 g PVDF (Sigma-Aldrich, average molecular weight ~534,000 by GPC, powder) and 0.086 g $NaNH_2$ (Sigma-Aldrich, 95%) was loaded into an alumina tube reactor located in a furnace, which was then vacuumized for 10 hrs. Afterwards, the mixture was annealed at 130 ºC for 2 hrs followed by 600 ºC for another 2 hrs under continuous vacuuming. After cooling down to room temperature, as-produced mixture was collected and dissolved in 3 mL absolute ethanol (Decon Laboratories, Inc., 200 Proof). The ethanol suspension was ultrasonicated for 5 min in an ultrasonication bath, and then filtered with a 0.45 μm syringe filter.

***Material characterizations:*** The crystal structure of reactants and products was determined using a Scintag XDS2000 X-ray powder diffractometer. The molecular vibration of carbon chains in ethanol solution was detected by a Shimadzu IRAffinity-1 spectrometer with a liquid cell. The elemental composition of carbon chains was acquired with a Costech 4010 elemental analyzer. The morphology of carbon chains was revealed by an Omicron VT-STM-XA 650 scanning tunneling microscope. Prior to STM scan, the ethanol solution of carbon chains was treated by cycles of freeze-pump-thaw to eliminate air in the solvent. Afterwards, the ethanol solution was deposited on a clean HOPG substrate, and then the substrate was annealed in ultrahigh vacuum ($1.9 \times 10^{-9}$ torr) at 100 ºC for 1 hr to remove ethanol molecules. STM scan was conducted in ultrahigh vacuum ($1.9 \times 10^{-9}$ torr) at room temperature.

***In-situ diffuse reflectance infrared Fourier-transform spectroscopy:*** *In-situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was carried out on a Shimadzu IRAffinity-1 spectrometer with an *in-situ* diffuse reflection cell (DiffusIR, PIKE Technologies) which is equipped with a ZnSe window. The DRIFTS spectra were collected with 4 $cm^{-1}$ resolution and 45 scan numbers in the region from 600 to 4000 $cm^{-1}$. The KBr powder was dried, grinded, and pressed into a porous ceramic cup, after which 0.15 mL ethanol solution with carbon chains was dripped onto the KBr surface. The *in-situ* diffuse reflection cell was vacuumized for 2 hrs and then heated at 350 ºC for 2 hrs under continuous vacuuming to remove ethanol and any adsorbed impurities, leaving the pure carbon chains dispersed on KBr surface. Afterwards, the pure carbon chains were slowly heated at 2 ºC/min to 600 ºC under either continuous vacuuming or a 10 mL/min gas flow ($N_2$, $H_2$, $O_2$, or $CO_2$). The cell was cooled down after staying at 600 ºC for 1 hr.

***Density functional theory calculations:*** Density functional theory (DFT) calculations were performed with Gaussian 16 package.[1] The Heyd-Scuseria-Ernzerhof hybrid functional was used with its fraction of exact exchange set as 0.8.[2, 3] Structure optimization and frequency calculations of polyyne (using a diatomic unit cell) and cumulene (using a monoatomic unit cell) were conducted employing periodic boundary conditions with 6-31G(D) basis set. The absence of imaginary frequency was ensured, and the scaling factor of frequency is set as 0.951. The STM image of polyyne was simulated using Multiwfn 3.8 (dev) code.[4]

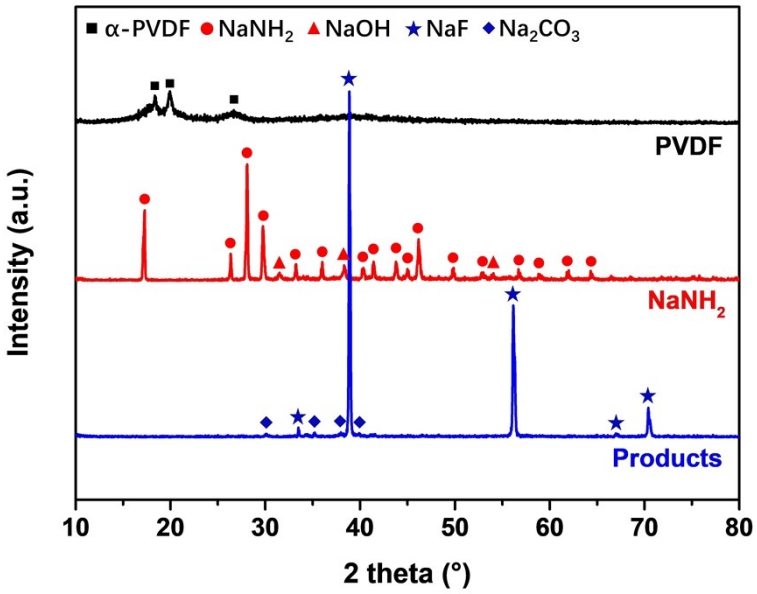


**Fig. S1** XRD patterns of PVDF, $NaNH_2$, and the produced mixture after reaction. Note: The scarce amount of $Na_2CO_3$ in the produced mixture was derived from the NaOH impurity in $NaNH_2$.

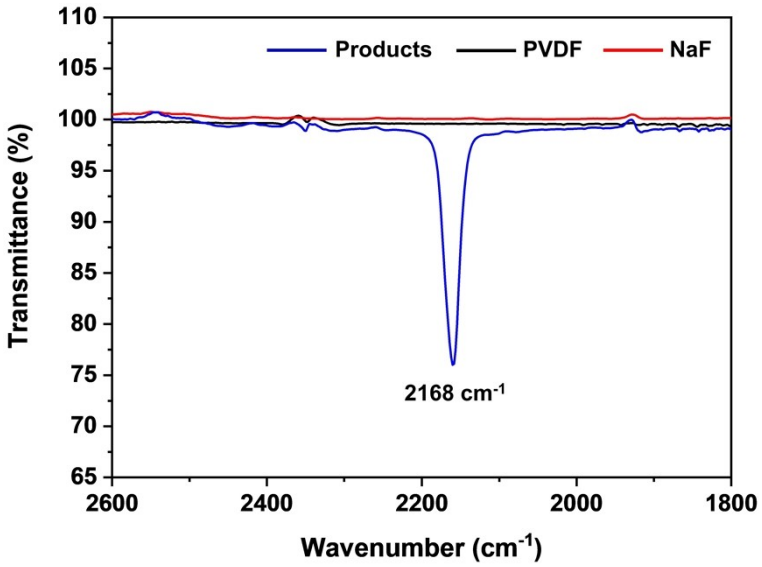


**Fig. S2** FT-IR spectra of ethanol solutions obtained by dissolving the produced mixture, PVDF, and NaF in ethanol followed by filtration to remove the insoluble solids. Note: Pure ethanol was used as the background.

**Table S1** DFT calculation results of polyyne and cumulene.

| Parameter | Polyyne | Cumulene |
|---|---|---|
| Bond length (Å) | 1.1966 and 1.3474 | 1.2610 |
| Energy per atom (eV) | -1040.6222 | -1040.4943 |
| Frequency ($cm^{-1}$) | 2179 | None |

**Table S2** Attenuation degree of the DRIFTS signal of carbon chain stretching vibration after the heating-cooling process (heating from room temperature to 600 ºC and then cooling to room temperature).

| Condition | Attenuation degree |
|---|---|
| Vacuum - cycle 1 | 44% |
| Vacuum - cycle 2 | 42% |
| $N_2$ flow | 1% |
| $H_2$ flow | 42% |
| $O_2$ flow | 99% |
| $CO_2$ flow | 47% |

**Supplementary References**


1. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, Gaussian 16.
2. S. Fang and Y. H. Hu, *Carbon*, 2021, **171**, 96-103.
3. K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross and H. L. Anderson, *Science*, 2019, **365**, 1299-1301.
4. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.