High Selectively C_2H_4/C_2H_2 Separation by cyano-functionalized alkadiyne-pyrene conjugated frameworks membrane

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PS1: The OPLS-AA force-field parameters for PTEP, CN-PTEP, gas molecules, and graphene.

The PTEP and CN-PTEP membranes were described within the OPLS-AA framework, in which membrane atoms were assigned Lennard-Jones (LJ) parameters and partial charges according to their local chemical environments. As shown in Fig. S1a-b and Table S1, the pristine PTEP membrane contains one labeled hydrogen site (H) and three labeled carbon sites (C1, C2, and C3). Specifically, H denotes the hydrogen atom attached to the benzene ring, C1 refers to the carbon atom in the benzene ring bonded to H, C2 denotes a carbon atom in the benzene ring, and C3 denotes a carbon atom in the alkynyl chain. For the CN-functionalized membrane, N1 denotes the nitrogen atom in the -CN group, C1 denotes the carbon atom in the -CN group, C2 denotes the carbon atom in the benzene ring directly bonded to the -CN group, C3 denotes a carbon atom in the benzene ring, and C4 denotes a carbon atom in the alkynyl chain. The gas molecules C_2H_2 and C_2H_4 were also described using the OPLS-AA force field, and the corresponding parameters are summarized in Table S1.

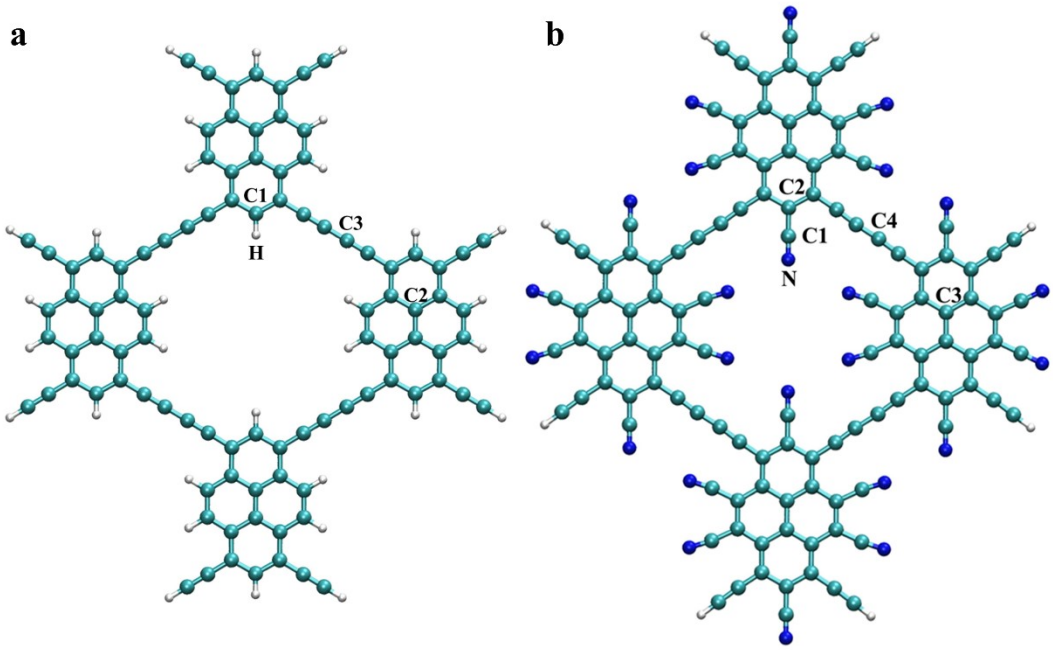

Fig. S1 Atom-type assignment for the PTEP and CN-PTEP membranes. Atoms are colored as follows: C, cyan; H, white; N, blue.

Table R1. The OPLS-AA force-field parameters used for PTEP, CN-PTEP, C_2H_2, and C_2H_4 in the MD simulations.

Molecule	Atom type	ε(kJ/mol)	σ(Å)	q(e)	Ref
PTEP	C1	0.293	3.550	-0.115	1
	C2	0.293	3.550	0.000	1
	C3	0.360	3.400	0.000	2
	H	0.126	2.420	0.115	1
CN-PTEP	C1	0.628	3.650	0.395	3
	C2	0.293	3.550	0.035	3
	C3	0.293	3.550	0.000	1
	C4	0.360	3.400	0.000	2
	N	0.711	3.200	-0.430	3
C_2H_2	C	0.360	3.300	-0.294	4
	H	0.063	2.420	0.294	4
C_2H_4	C	0.318	3.550	-0.330	4
	H	0.126	2.420	0.165	4
graphene	C	0.293	3.400	0.000	5

PS2: Definition of C-H···N hydrogen bonding and analysis of the most stable adsorption configurations of C_2H_4 and C_2H_2 on CN-PTEP.

According to previous studies[6, 7] and the IUPAC[8] recommendation, a C-H···N interaction can be considered to form hydrogen bond when the H···N distance is within the sum of the van der Waals radii of H and N and the C-H···N angle is larger than 110°. For the present system, we therefore considered the H···N distances and the ∠C-H···N angles between C_2H_4/C_2H_2 and the cyano functional groups inside the pore. Using the commonly adopted van der Waals radii of 1.20 Å for H and 1.55 Å for N, the corresponding H···N distance is 2.75 Å.

As shown in Fig. S2, for the most stable adsorption configuration of C_2H_4 adsorption on the CN-PTEP membrane, the H1···N1 distance was 2.46 Å and the angle ∠C1-H1···N1 was 162.4°, the H2···N2 distance was 2.41 Å and the angle ∠C1-H2···N2 angle was174.6°, which indicate two C-H···N hydrogen bonds formed between C_2H_4 and CN-PTEP. In contrast, for the most stable adsorption configuration of C_2H_2 adsorption on the CN-PTEP membrane, the H1···N1 and H1···N2 distances increase to 3.57 and 3.47 Å, respectively, while the corresponding ∠C1-H1···N1 and ∠C1-H1···N2 angles decrease to 111.8° and 113.8°, which indicates C_2H_2 cannot form C-H···N hydrogen bond with CN-PTEP membrane.

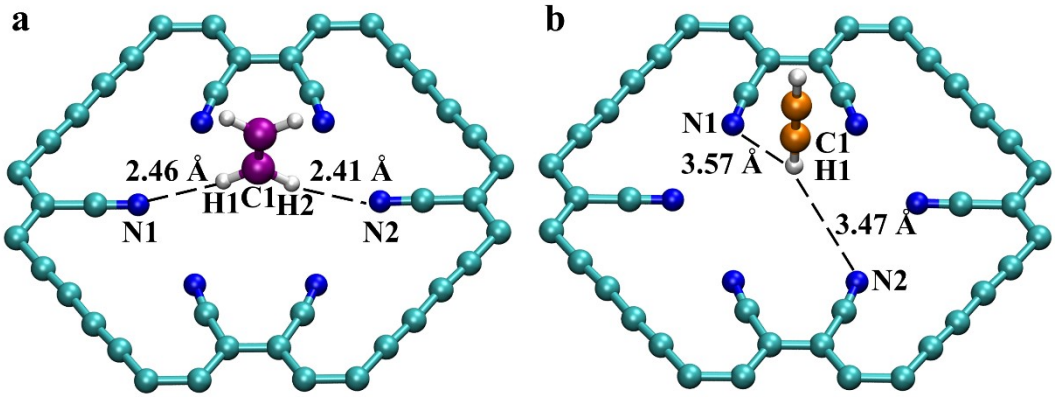

Fig. S2 Optimized configurations of C_2H_4 and C_2H_2 adsorption on the CN-PTEP membrane. Atoms are colored as follows: C, cyan; H, white; N, blue. For clarity, the carbon atoms of C_2H_4 are colored purple, and the carbon atoms of C_2H_2 are colored orange.

PS3: Other adsorption configurations and adsorption energies of gas molecules on the CN-PTEP and PTEP membranes.

Fig. S3 shows the different adsorption configurations of ethylene (C_2H_4) and acetylene (C_2H_2) molecules on the CN-PTEP membrane, where d represents the perpendicular distance of the gas molecules from the membrane surface.

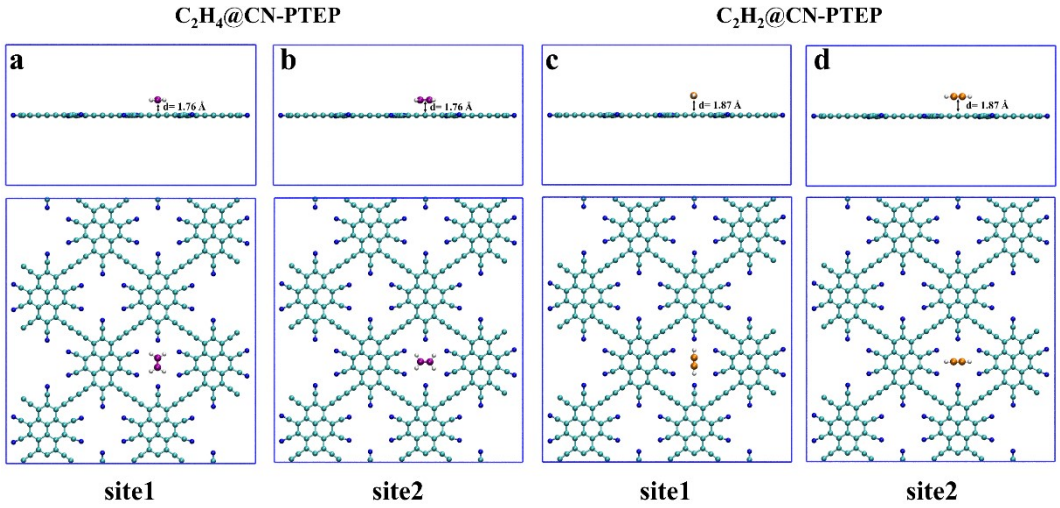

Fig. S3 Adsorption configuration of C_2H_4 and C_2H_2 on CN-PTEP membrane. The different adsorption configurations of C_2H_4 molecules (a-b) and C_2H_2 molecules (c-d) on CN-PTEP membranes, as well as their vertical heights relative to the membrane surface. Atoms are colored as follows: C, cyan; H, white; N, blue. For clarity, the carbon atom of C_2H_4 is colored purple, and the carbon atom of C_2H_2 is colored orange.

As shown in Fig. S4, the most stable adsorption configuration of C_2H_4 was oriented horizontally at the center of the membrane pore (Fig. S4a), while C_2H_2 was adsorbed vertically at the pore center and aligned perpendicular to the PTEP membrane plane (Fig. S4i).

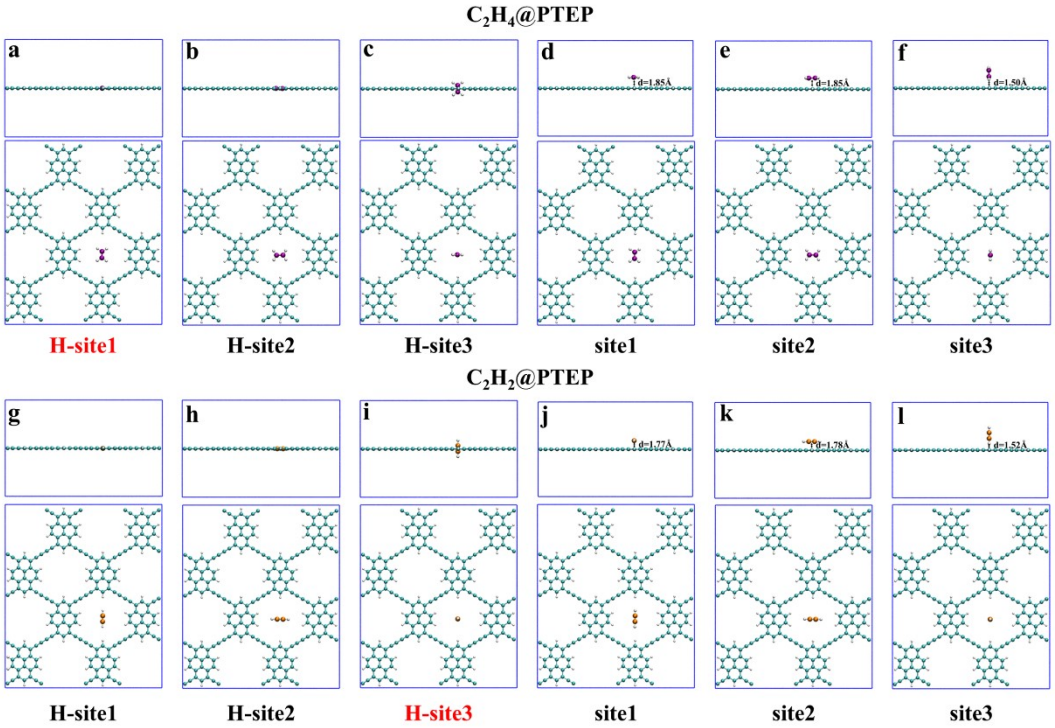

Fig. S4 Adsorption configuration of C_2H_4 and C_2H_2 on PTEP membrane. The different adsorption configurations of acetylene molecules (a-f) and ethylene molecules (g-l) on PTEP membranes, as well as their vertical heights relative to the membrane surface. Atoms are colored as follows: C, cyan; H, white; N, blue. For clarity, the carbon atom of C_2H_4 is colored purple, the carbon atom of C_2H_2 is colored orange.

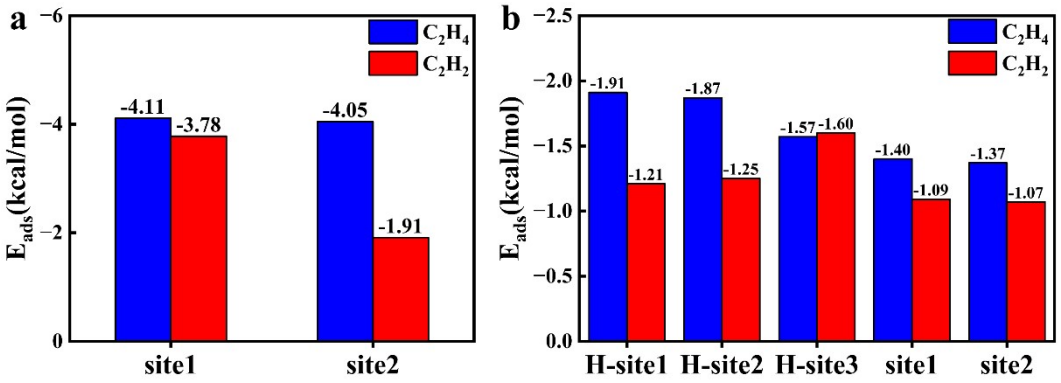

Fig. S5 Adsorption energies of C_2H_4 and C_2H_2 on CN-PTEP and PTEP membranes with different adsorption configurations. (a) Adsorption energies on the CN-PTEP membrane;(b) Adsorption energies on the pristine PTEP membrane.

PS4: Transition-state interaction analysis for C_2H_4 and C_2H_2 permeation through the CN-PTEP pore.

We further analyzed the transition-state geometries and pore-molecule interactions in detail. The pore-molecule interaction at the transition state was defined as follows:

$$E_{int} = E_{TS} - E_{CN\text{-}PTEP} - E_{gas}$$

where E_{TS} is the total energy of the transition-state configuration, $E_{CN\text{-}PTEP}$ is the energy of the CN-PTEP membrane, and E_{gas} is the energy of the gas molecules.

The interaction energy between C_2H_4 and CN-PTEP at the TS is -4.09 kcal/mol, this attraction interaction mainly results from the C-H···N hydrogen bond formed between C_2H_4 and CN-PTEP, thus the energy barrier of C_2H_4 is very small. Whereas the interaction of C_2H_2 is 2.63 kcal/mol, which shows that C_2H_2 was repelled when passing through the pore, thus the relatively high energy barrier needs to be overcome.

As shown in Fig. R5, the H1···N1 distance was 2.44 Å and the angle ∠C1-H1···N1 was 134.3°, and the H2···N2 distance was 2.44 Å and the angle ∠C1-H2···N2 angle was137.4°, which indicates two C-H···N hydrogen bonds formed between C_2H_4 and CN-PTEP. In contrast, for C_2H_2, the H1···N1 and H1···N2 distances increase to 3.63 and 3.72 Å, respectively, while the corresponding ∠C1-H1···N1 and ∠C1-H1···N2 angles decrease to 64.7° and 63.6°, which indicates C_2H_2 cannot form C-H···N hydrogen bond with the CN-PTEP membrane. C_2H_4 formed two C-H···N hydrogen bonds with the CN-PTEP membrane, which results in the favorable orientation of C_2H_4 to pass through the nanopore of CN-PTEP. However, C_2H_2 without C-H···N hydrogen bond passes vertically through the nanopore of the CN-PTEP. These results showed that the selective permeation of C_2H_4 arises from the C-H···N hydrogen-bonding interaction and the resulting favorable orientational.

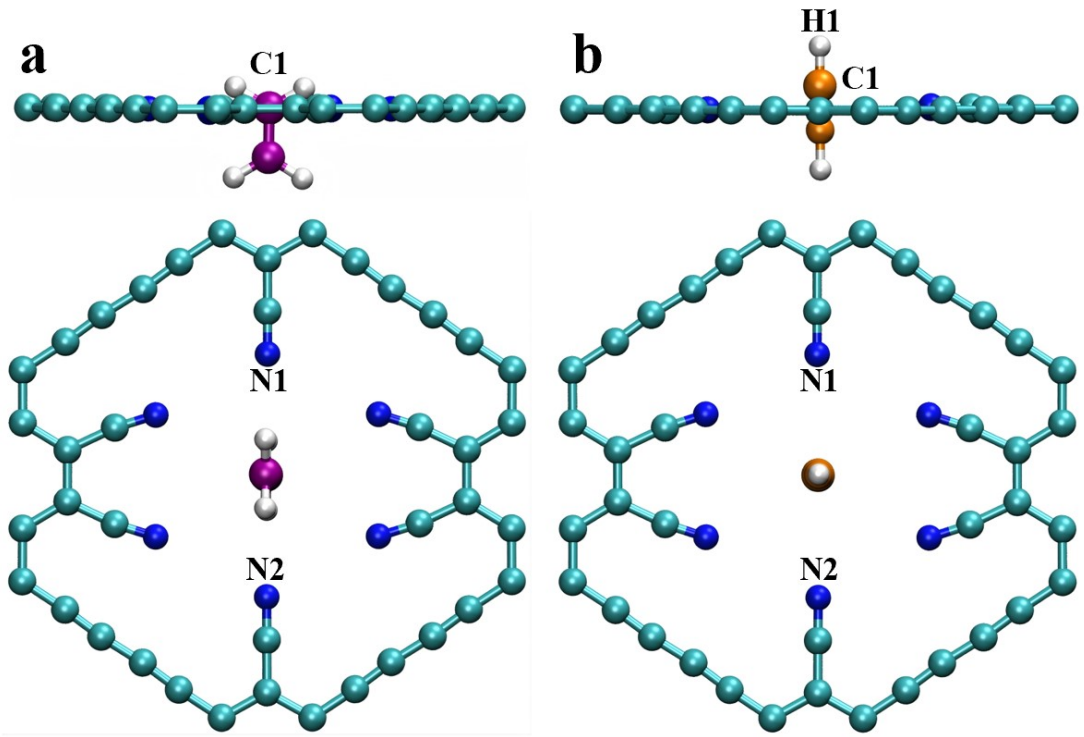

Fig. S6 Transition-state configurations of C_2H_4 and C_2H_2 permeation through the CN-PTEP pore. Atoms are colored as follows: C, cyan; H, white; N, blue. For clarity, the carbon atoms of C_2H_4 are colored purple, and the carbon atoms of C_2H_2 are colored orange.

PS5: The estimation of pre-exponential factors for C_2H_4 and C_2H_2 based on transition-state theory.

We have performed vibrational frequency analyses for both the initial states (IS) and transition states (TS) of C_2H_4 and C_2H_2 permeation, and estimated the pre-exponential factors based on the transition-state theory (TST). According to the previous research[9], the pre-exponential factor was calculated as follows:

$$A_{act} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{k_B}\right) \quad (4)$$

where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, $\Delta S^{\ddagger}$ is the activation entropy defined as S_{TS} - S_{IS}.

Table S2 The pre-exponential factors based on TST, diffusion barriers, and corrected ideal selectivity for C_2H_4/C_2H_2 permeation through the CN-PTEP membrane at 298 K.

gas	A (s^{-1})	E_b (kcal/mol)	selectivity
C_2H_4	4.15×10^{12}	0.87	1×10^{4}
C_2H_2	1.05×10^{13}	6.87	

PS6: Effect of ESP-derived pore-edge charges on the MD permeation results.

To assess the possible influence of the pore-edge electrostatic environment on the MD results, we further examined the effect of ESP-derived charges for representative pore-edge atoms in the CN-PTEP membrane. The original MD simulations were carried out using the charge parameters provided by the OPLS-AA force field. To refine the electrostatic description around the pore edge, a representative cluster model of the CN-PTEP pore region was constructed, as shown in Fig. S7a. Based on this cluster model, DFT calculations were performed using Gaussian[10] at the B3LYP/6-31G(d) level[11], and the electrostatic potential (ESP) charges of the key pore-edge atoms were subsequently obtained using the Multiwfn program[12].

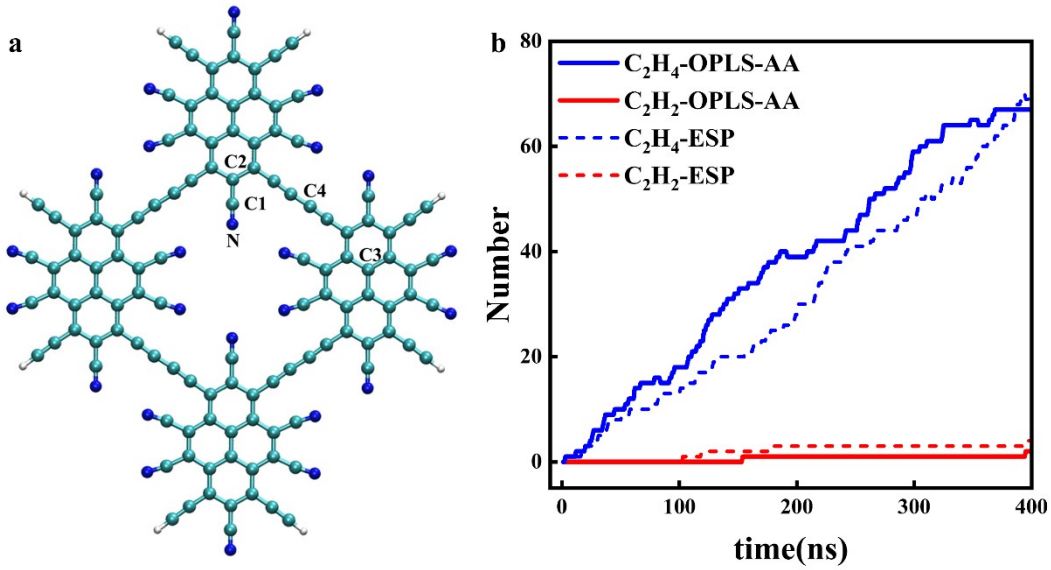

Fig. S7 ESP charge derivation and MD validation for the CN-PTEP pore. (a) Representative cluster model of the CN-PTEP pore used for DFT-based ESP charge analysis. N1 denotes the nitrogen atom in the -CN group, C1 denotes the carbon atom in the -CN group, C2 denotes the carbon atom in the benzene ring bonded to the -CN group, C3 denotes a carbon atom in the benzene ring, and C4 denotes a carbon atom in the alkynyl chain.(b) Time evolution of permeated molecule numbers at 298 K obtained using the original OPLS-AA charges (solid lines) and the ESP-derived charges (dashed lines). Atoms are colored as follows: C, cyan; H, white; N, blue.

The resulting ESP-derived charges were compared with the original charge

parameters used in the MD simulations, and the detailed comparison is summarized in Table S3. For the representative pore-edge atoms, the original/ESP-derived charges are 0.395/0.382 for C1, 0.035/0.023 for C2, 0/0 for C3, 0/0 for C4, and -0.430/-0.405 for N, respectively. Although the absolute magnitudes are slightly reduced in the ESP-derived values, the charge signs and the relative electrostatic distribution around the pore are consistent.

To further evaluate whether this charge difference would affect the MD results, we further performed a validation simulation at 298 K by using the ESP-derived charges. As shown in Fig. S7b, compared with the original charge set, the number of permeated C_2H_4 molecules changed only slightly from 67 to 70, while that of C_2H_2 changed from 2 to 4 after the same 400 ns simulation time. Thus, the use of ESP-derived charges leads to minor quantitative variations and does not alter the qualitative permeation trend. In particular, CN-PTEP still exhibits a pronounced preferential permeation for C_2H_4 over C_2H_2.

Table S3 Original and ESP-derived charges of the key pore-edge atoms in CN-PTEP

Atom	C1	C2	C3	C4	N
OPLS-AA charge	0.395	0.035	0.000	0.000	-0.430
ESP-derived charge	0.382	0.023	0.000	0.000	-0.405

PS7: MD simulation model and the permeation behavior of the pristine PTEP membrane.

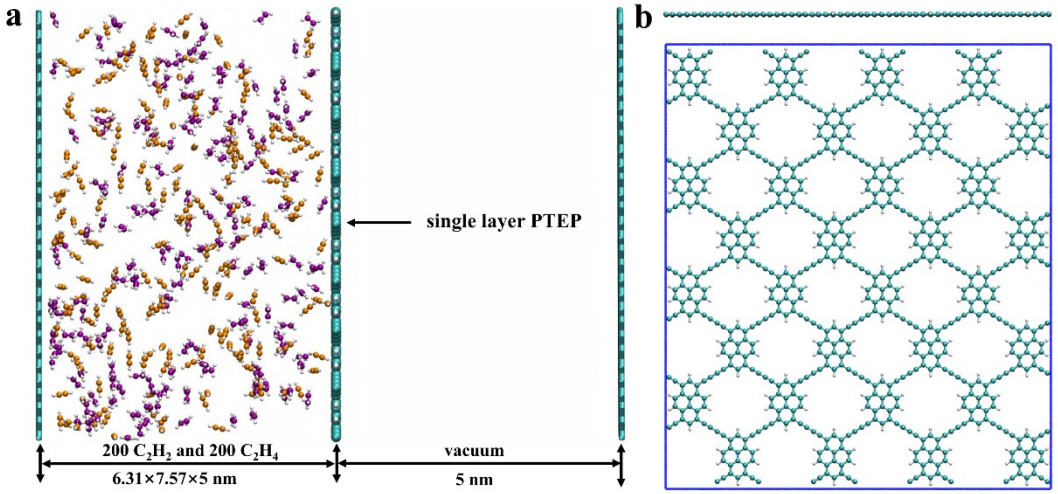

Fig. S8 MD simulation model and PTEP membrane structure for C_2H_4/C_2H_2 separation. (a) Simulation model of the C_2H_4/C_2H_2 mixture separation through the PTEP membrane. (b) Side and top views of the single-layer PTEP used in the simulations. Atoms are colored as follows: C, cyan; H, white. For clarity, the carbon atoms of C_2H_4 are colored purple, the carbon atoms of C_2H_2 are colored orange.

Fig. S9a showed the variation of the number of C_2H_4 and C_2H_2 passing through the PTEP membrane over time. Fig. S9b was a snapshot of the separation system at 500 ps. At this time, ~101 C_2H_2 and~99 C_2H_4 pass through the PTEP membrane.

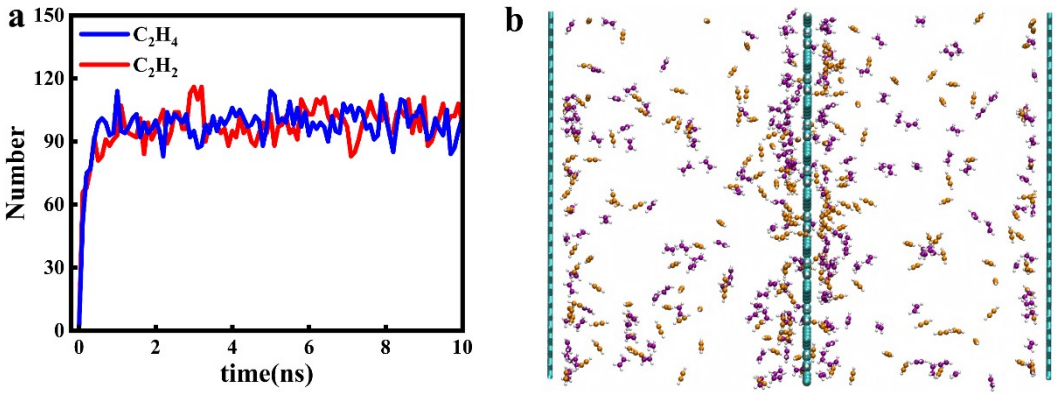

Fig. S9 Separation performance of the CN-PTEP membrane for C_2H_4/C_2H_2. (a) The number of gas molecules passing through the PETP membrane changed with simulation time. (b) Snapshots of the C_2H_4/C_2H_2 gas mixtures permeating through the PTEP membrane after 500 ps. Atoms are colored as follows: C, cyan; H, white. For clarity, the carbon atoms of C_2H_4 are colored purple, the carbon atoms of C_2H_2 are colored orange.

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