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

Supporting Information

Separation selectivity and structural flexibility of graphene-like 2-dimensional membranes

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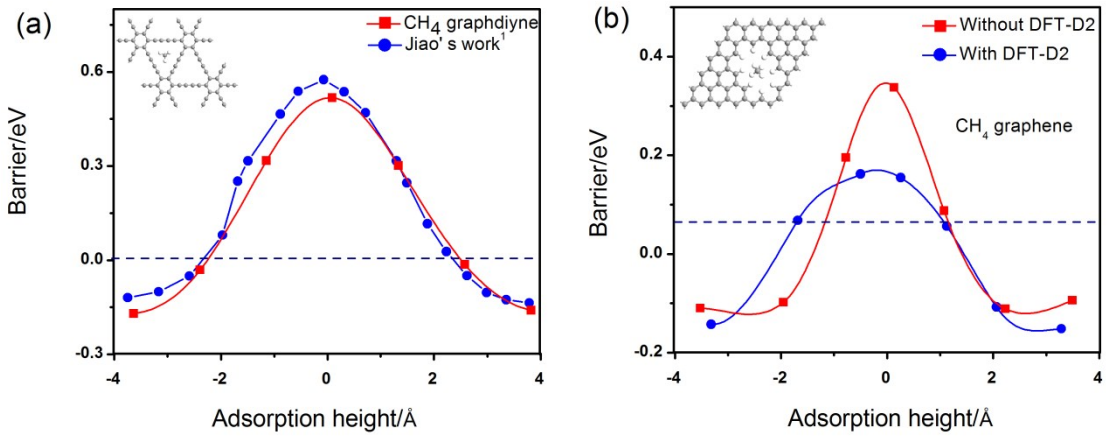

Fig. S1. Diffusion energetics of CH_4 penetrating membranes. (a) CH_4 passing through graphyne, calculated with the PBE functional. (b) CH_4 passing through porous graphene. The NEB method was coupled with the PBE functional (red) and with the DFT (PBE)-D2 functional (blue). Insets show the model with different passing molecules. The interaction energy is defined as E_{int} = E(total) - E(membranes) - E (CH_4). The adsorption height is the distance between the center of the molecule and the plane of membranes.

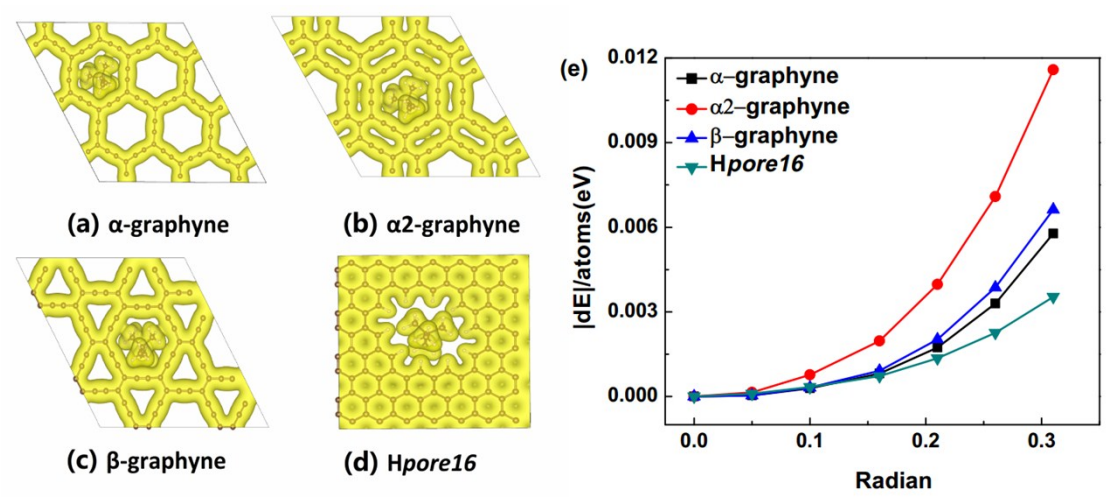

Fig. S2. Electron density plotof the graphyne membrances and neopentane *and* the rigidity of the *z*-direction deformation of the porous membranes. Neopentane is in the middle of the pore of membrances of (a) *α*-graphyne, (b) *α*2-graphyne, (c) *β*-graphyne and (d) H*pore16*. Eletron density isovalue is 0.02e/Å^3. (e) Energy change as a function of the *z*-direction deformation of the porous membranes.

We assumed that the membrances can be bent into different curvatures, which is more or less what the passing molecules do. The easiness to bend a membrane into different curvature represent its deformation capability (or rigidity) primarily in the *z*-direction or out-of-plane direction. By calculating the energy change after deformation (characterized by radian), we obtained the rigidity, which is in the order of *α*2-graphyne > *β*-graphyne > *α*-graphyne > H*pore16*.

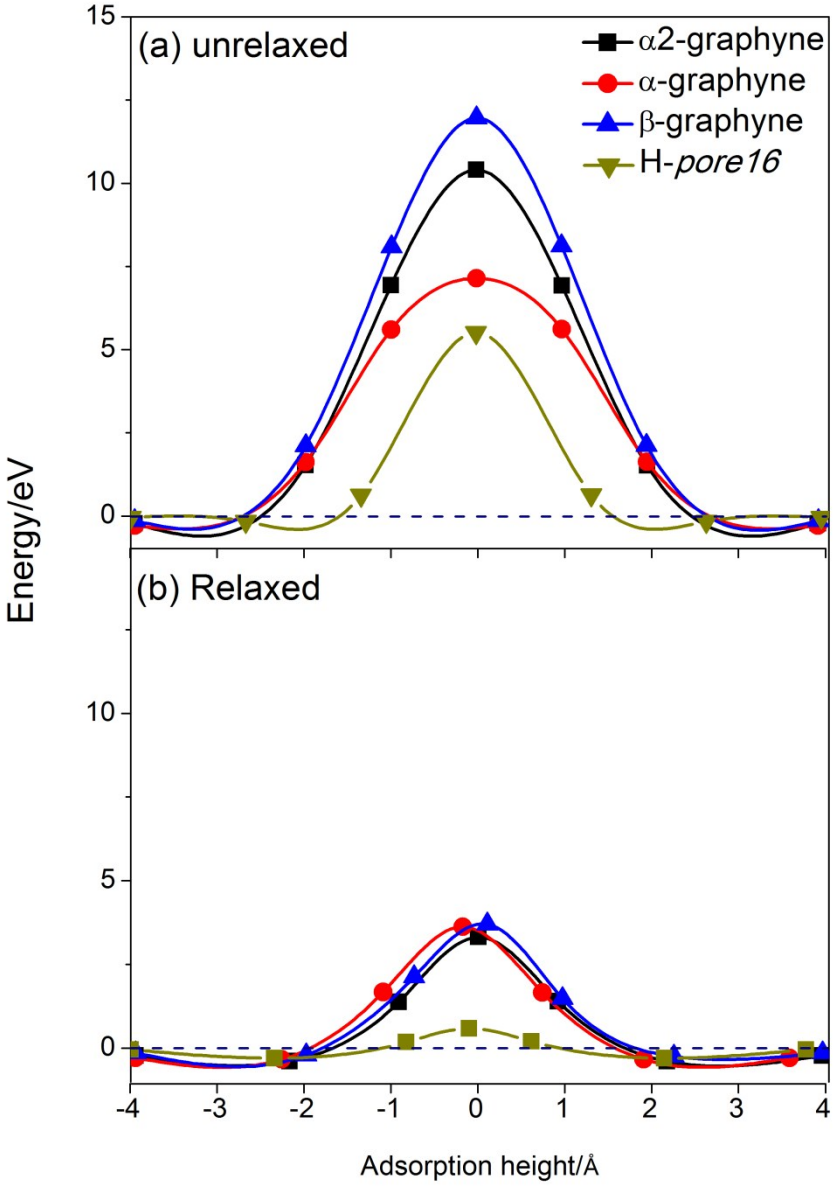

Fig. S3. Relaxed versus unrelaxed calculations. The diffusion energetics of neopentane passing through four porous models plotted as a function of the adsorption height. (a) Calculations using unrelaxed structures. (b) Calculations using relaxed structures.

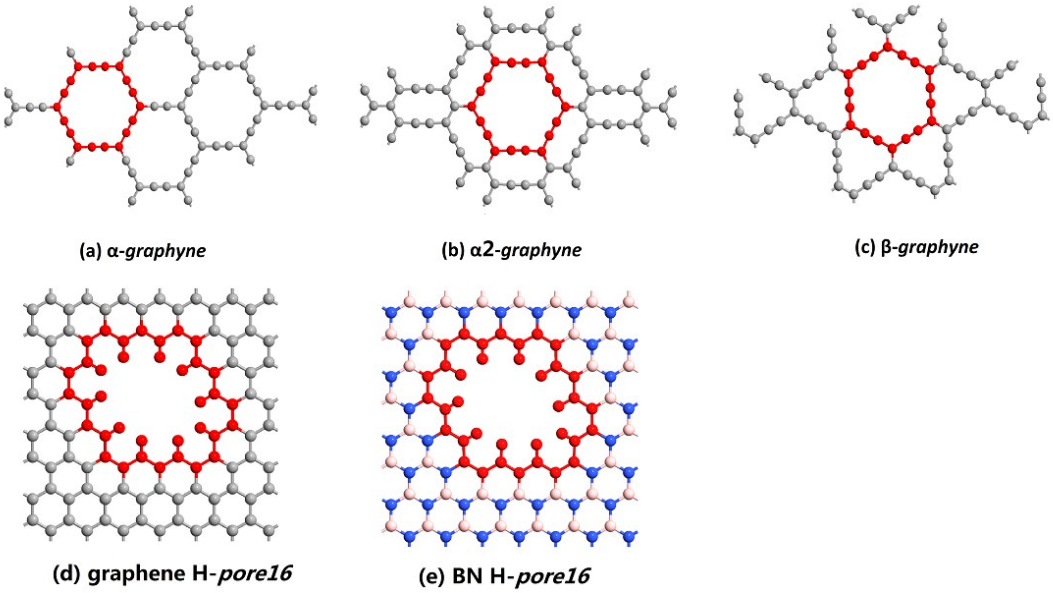

Fig. S4. Atoms used for calculating the graphene *z*-direction deformation. (a) *α*-graphyne, (b) *α*2-graphyne, (c) *β*-graphyne, (d)graphene *Hpore16,* and (d) BN *Hpore16*. Only the red atoms were used to calculate the *z*-direction deformation ($d|\bar{z}|$).

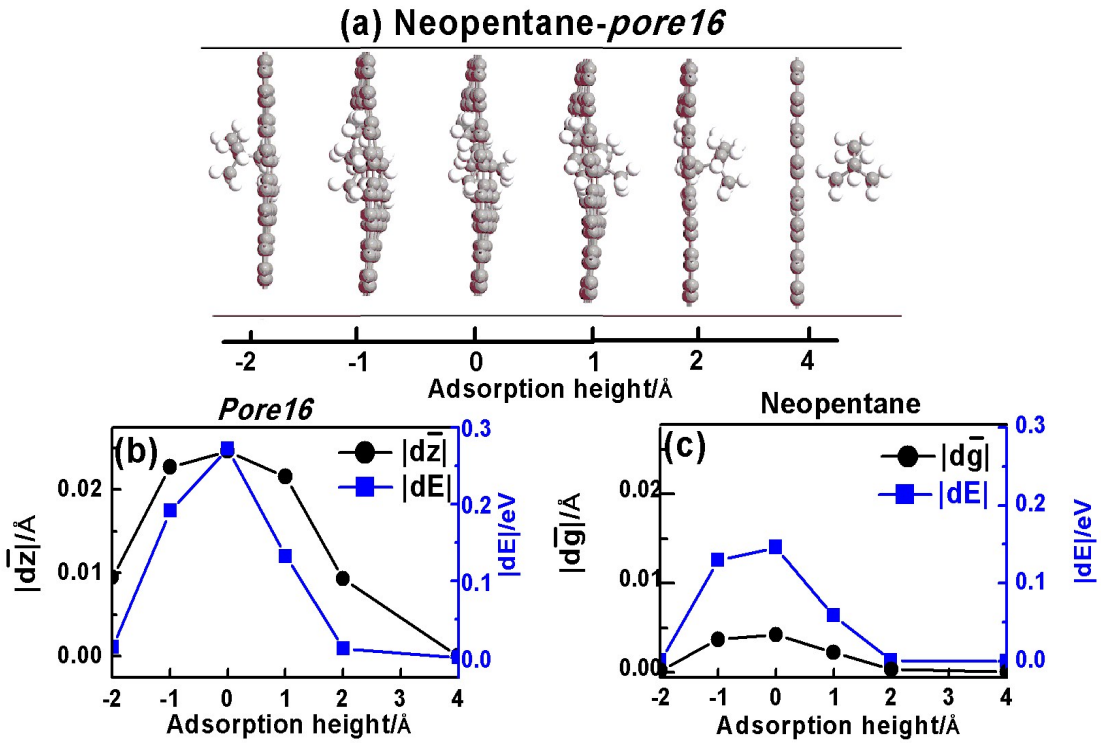

Fig. S5. Deformation analysis of neopentane passing through H*pore16*. (a) Snapshots. (b) The z-direction deformation ($d|\bar{z}|$) and the energy change (|dE|) of H*pore16*. (c) The atomic displacement ($d|\bar{g}|$) and the energy change (|dE|) of neopentane as a function of adsorption height.

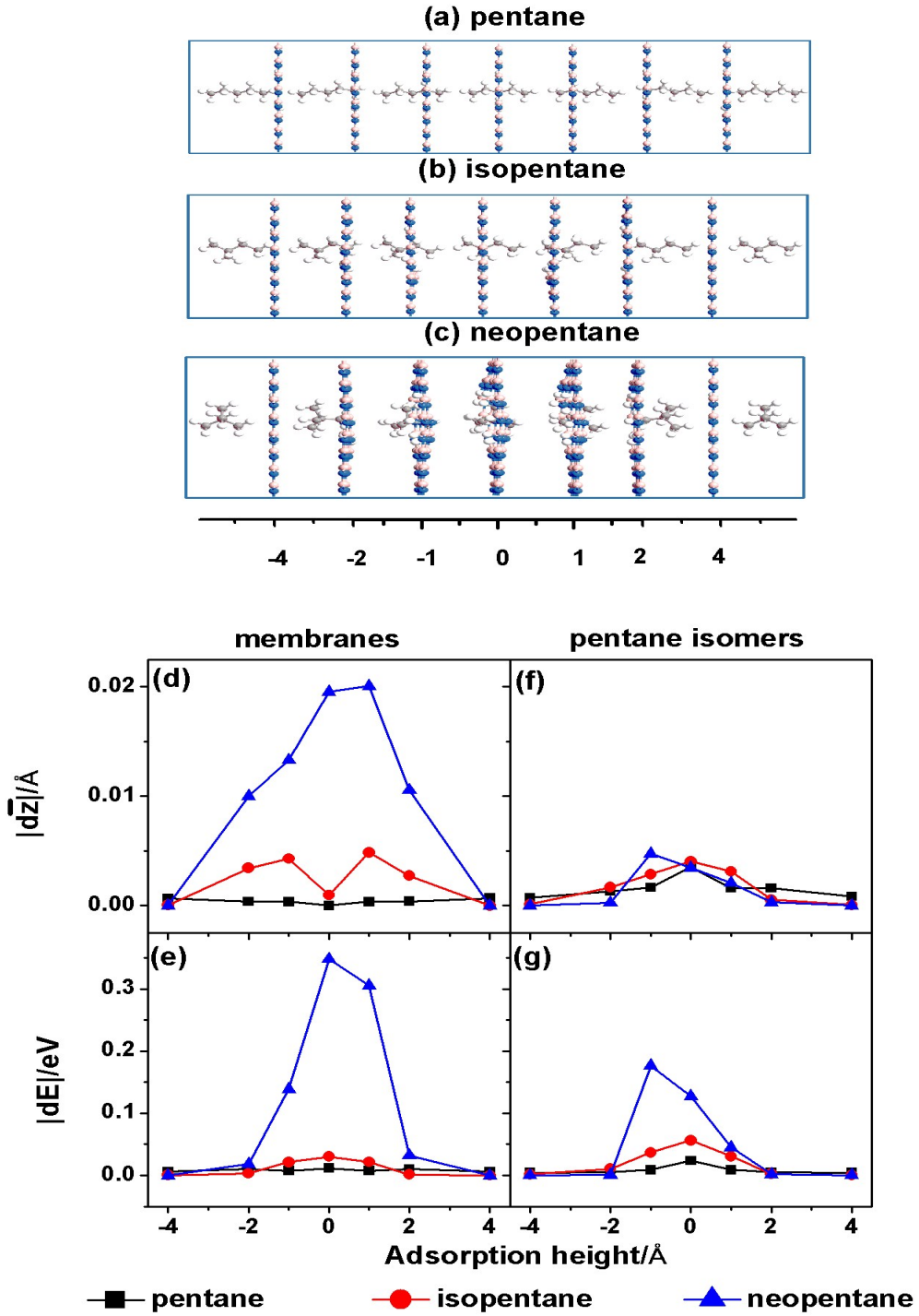

Fig. S6. Deformation analysis of pentane isomers passing through BN H*pore16*. Snapshots of (a) pentane, (b) isopentane, and (c) neopentane passing through BN H*pore16*. (d) The z-direction deformation ($d|\bar{z}|$) and(e) the energy change (|dE|) of BN H*pore16* due to the isomers. The structure deformation (g) and energy changes of pentane isomers (f).

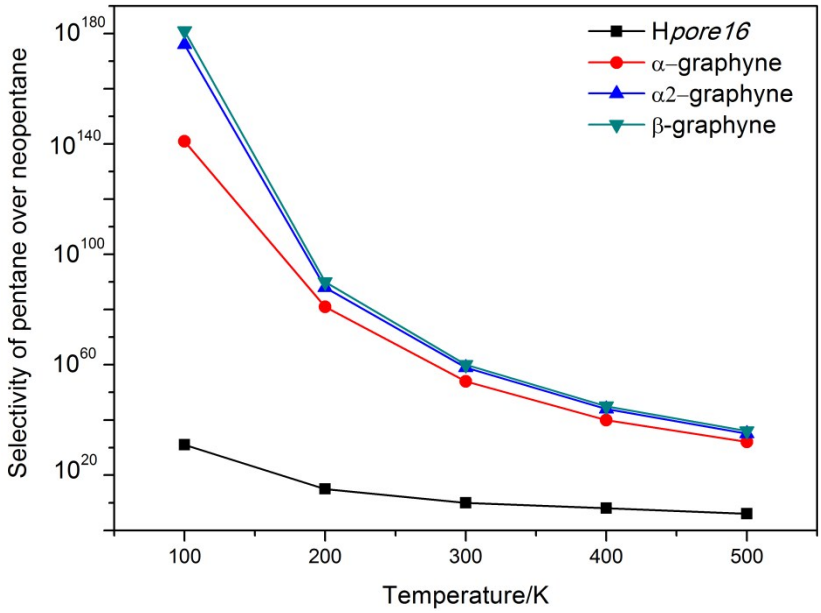

Fig. S7. Temperature effect on the selectivity of pentane over neopentane.

Table S1. The frequency of transition state as isopentane and neopentane passing through the α and β-graphyne sheets.

Frequency/cm^{-1}			
Isopentane α-graphyne	neopentane α-graphyne	Isopentane β-graphyne	neopentane β-graphyne
-68.2	-98.3	-95.3	-103.6
-0.2	-10.2	-0.3	-0.5
-0.1	-0.2	-0.2	-0.2
0.1	0.2	-0.1	0.3
13.9	0.4	24.3	2.6
30.6	2.8	30.0	17.2
32.5	15.2	34.8	25.0
35.0	20.7	37.7	33.3
37.7	30.4	38.3	36.8
39.1	31.9	47.5	43.6
42.0	36.6	52.4	69.6
44.4	37.9	67.9	76.9
60.3	47.0	78.0	85.1
62.2	48.0	82.3	87.2
66.4	54.9	87.6	89.9
67.3	60.7	95.5	94.2
73.0	66.9	99.2	96.6
77.1	71.6	107.8	104.3
81.3	76.5	110.5	111.3
92.2	91.4	113.1	112.2
93.7	94.6	116.3	114.2
115.1	100.0	119.5	118.2
116.5	102.4	123.7	118.9
119.5	109.5	131.2	127.7
124.8	111.5	133.2	140.1
126.7	118.3	137.8	143.8
128.8	120.9	150.4	154.2
133.4	129.6	154.1	162.0
137.9	136.1	165.0	169.0
147.0	156.6	169.2	179.4
160.8	159.7	173.0	180.5
164.1	165.1	176.3	185.3
178.5	170.5	179.9	191.8
180.5	175.5	183.4	197.8
183.0	179.9	188.0	199.3
186.2	183.4	190.5	201.6
188.6	189.0	193.5	207.7

191.3	194.0	197.1	212.8
194.4	196.4	205.5	216.6
201.0	198.3	212.8	222.6
206.9	204.0	215.5	228.8
210.2	209.7	217.8	230.8
220.0	213.8	236.9	250.2

Table S2. Pore diameters as neopentane passing through α-graphyne. The longest l and the shortest s diameters, and the average pore size [$\frac{1}{2}(l+s)$] as neopentane passing through α-graphyne.

Pore diameters	Adsorption height/Å				
	-2	-1	0	1	2
L	8.03	7.90	8.00	8.11	8.04
S	7.04	7.33	7.30	7.07	7.03
$\frac{1}{2}(l+s)$	7.53	7.61	7.65	7.59	7.53

References

1. Y. Jiao, A. Du, M.Hankel, Z. Zhu, V. Rudolph and S. C. Smith, *Chem.Commun.,* 2011**, 47**, 11843-11845.

2. A. W. Hauser and P. Schwerdtfeger, *Phys. Chem. Chem. Phys.*, 2012, **14** , 13292-13298.