Supplementary Material

Separation of CO_2/CH_4 gas mixtures using nanoporous graphdiyne and boron-graphdiyne membranes: influence of the pore size

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Table S1. Calculated adsorption energy E_{ads} and energy accuracy ΔE for three calculations (n = 1-3) of the adsorption of CO_2 on GDY in which the grid of k points in the first Brillouin zone is fixed and the cut-off energy is varied (upper part of the Table), and for three calculations in which the cut-off energy is fixed and the grid of k points is varied (lower part of the Table). ΔE is calculated as $\Delta E(n)=E_{ads}(n+1)-E_{ads}(n)$. The meaning of ΔE is the numerical accuracy of the calculation with respect to the variable tested, namely cut-off energy (upper part) and grid of k points (lower part).

n	cut-off (Ry)	grid of k points	E_{ads} (eV)	ΔE (eV)
n = 1	35	2×2×1	0.1709	-3.1×10^{-3}
n = 2	45	2×2×1	0.1677	5.2×10^{-5}
n = 3	55	2×2×1	0.1678	
n = 1	45	1×1×1	0.1698	-2.0×10^{-3}
n = 2	45	2×2×1	0.1677	-2.0×10^{-4}
n = 3	45	3×3×1	0.1675	

Table S1 shows that the values of the parameters selected in this work, a cut-off energy of 45 Ry and a 2×2×1 grid of K points, yield well converged adsorption energies with a maximum numerical error of 2.0×10^{-4} eV.

Table S2. Calculated selectivity $S(CO_2/CH_4)$ of the GDY membrane for different tremperatures.

T(K)	$S(CO_2/CH_4)$
100	3.904×10^{11}
150	5.341×10^{17}
200	6.248×10^{5}

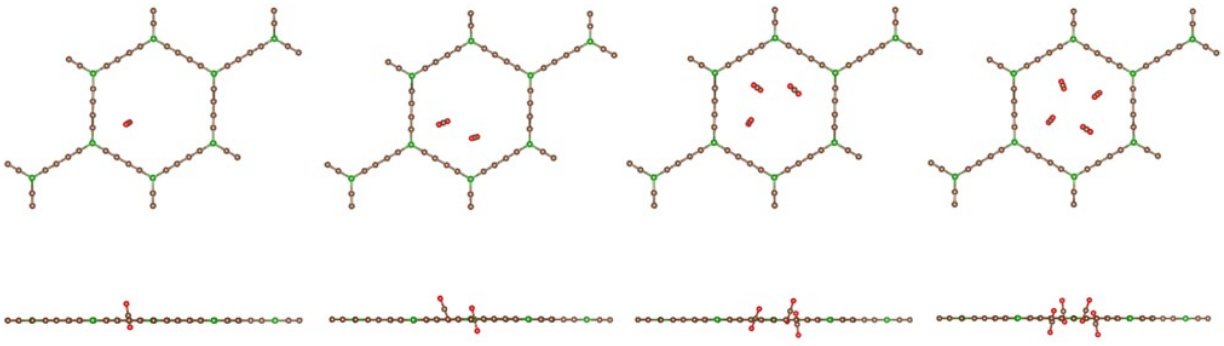
250	4.331×10^4
273	1.762×10^4
300	7.309×10^3
350	2.050×10^3
400	7.904×10^2
450	3.766×10^2
500	2.081×10^2

Adsorption of several CO_2 and CH_4 molecules on GDY and BGDY

Figure S1 shows the calculated lowest energy structures for the adsorption CO_2 and CH_4 molecules on BGDY. Up to four CO_2 molecules can be adsorbed, per hexagon, and these molecules sit practically on the plane of the BGDY layer, at positions midway between the center of the hexagon and the vertices, or the sides, of the hexagon. The orientation of the molecules is near-perpendicular to the BGDY layer. The CH_4 molecules occupy similar positions on BGDY, with the difference that only three molecules can be adsorbed.

The adsorption on GDY is more restrictive (see Fig. S2). Only one CO_2 molecule fits well in the triangular hole, above the layer plane, because of the smaller size of the pore hole. and a second molecule sits above a carbon chain which forms one side of the triangular hole. The orientation of the axis of the molecules is tilted with respect to the GDY plane. In a similar way, one CH_4 molecule is adsorbed above the center of the triangular hole, but the position of a second molecule is displaced towards a carbon hexagon on one vertex of the triangular hole. Figure S3 shows two examples of mixed adsorption.

(a) BGDY-nCO_2



(b) BGDY-nCH_4

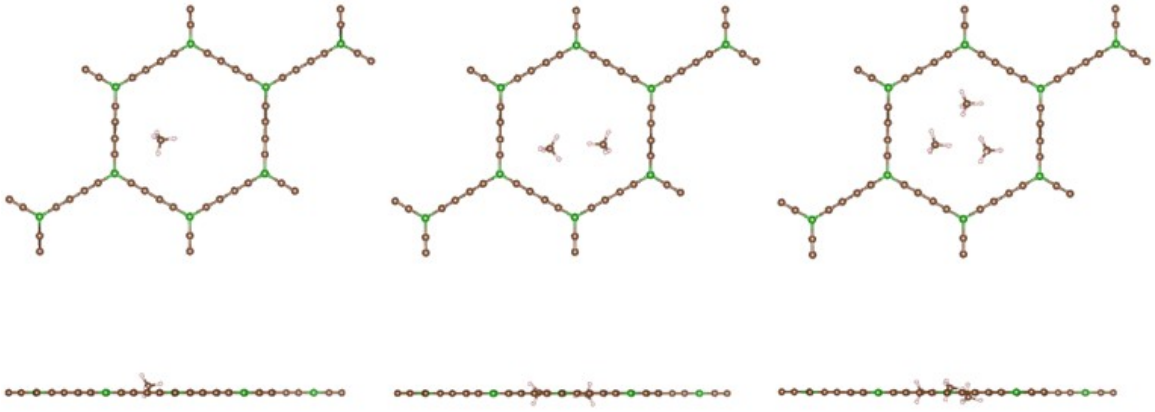


Figure S1. Calculated lowest energy structures for the adsorption CO_2 (panel a) and CH_4 molecules (panel b) on BGDY.

(a) GDY-nCO_2 (b) GDY-nCH_4

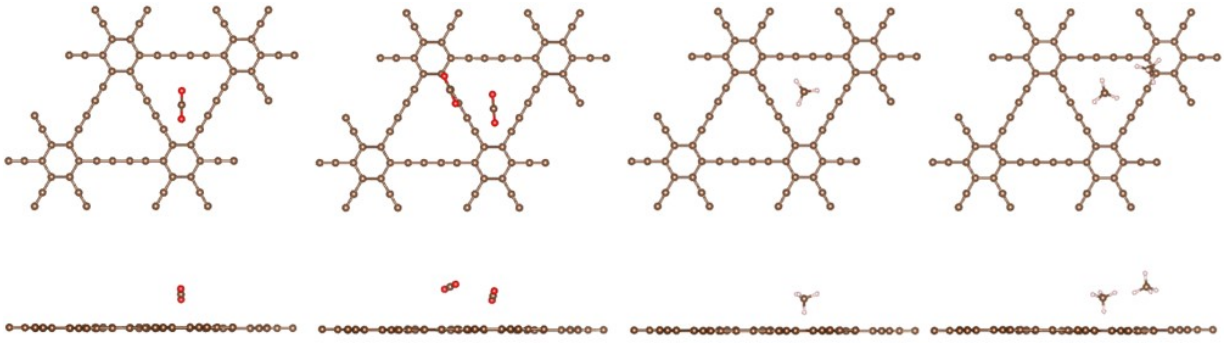


Figure S2. Calculated lowest energy structures for the adsorption CO_2 (panel a) and CH_4 molecules (panel b) on GDY.

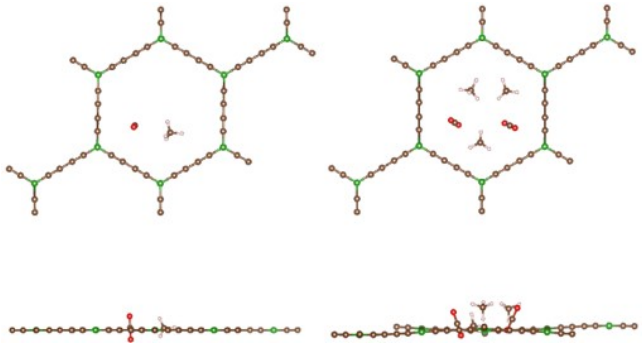


Figure S3. Calculated lowest energy structures for the adsorption of one CO_2 and one CH_4 molecules (left panel), and two CO_2 and three CH_4 molecules (right panel) on GDY.