Supplementary Information for

Interactions Between Dehydrobenzo[12]annulene (DBA) and Gas Molecules: Do the Preorganized Acetylenes Work Cooperatively?

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Computational methods

The Gaussian 03 programs were used for the *ab initio* molecular orbital calculations.[S1] Dunning's correlation consistent basis sets (aug-cc-pVDZ and aug-cc-pVTZ)[S2,S3] and 6-31G* basis set were used. Electron correlation was accounted for by the second-order Mϕller-Plesset perturbation (MP2) method[S4,S5] and by coupled cluster calculations with single and double substitutions with noniterative triple excitations [CCSD(T)].[S6] Basis set superposition error (BSSE) was corrected for by the counterpoise method.[S7,S8] The geometries of monomers were optimized at the MP2/ 6-311G** level with imposing D_{3h}, D_{6h}, and $D_{\infty h}$ symmetry. The optimized geometries were used for the calculations of the interaction energies without further geometry optimizations. The MP2 level interaction energy at the basis set limit [$E_{MP2(limit)}$] was estimated by the method of Helgaker *et al.*[S9] from the calculated MP2 interaction energies using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. In the method of Helgaker *et al.*, the calculated MP2 interaction energies with the Dunning's correlation consistent basis sets were fitted to the form $a + b X^{-3}$ (where X is 2 for aug-cc-pVDZ, 3 for aug-cc-pVTZ). The $E_{MP2(limit)}$ was then estimated by extrapolation.[S10] Helgaker's method was originally proposed for an estimation of electron correlation contribution at the basis set limit. But we used this method for an estimation of $E_{MP2(limit)}$, since the two basis sets provided nearly the same HF level interaction energies. The CCSD(T) level interaction energy at the basis set limit [$E_{CCSD(T)(limit)}$] was calculated as the sum of the $E_{MP2(limit)}$ and the estimated CCSD(T) correction term [$\Delta CCSD(T) = E_{CCSD(T)} - E_{MP2}$] at the basis set limit [ΔCCSD(T)(limit)], which was estimated from the difference between the calculated CCSD(T) and MP2 level interaction energies using the 6-31G* basis set.[S11,S12] The aug-cc-pVDZ basis set was used for the estimation of the ΔCCSD(T) for the benzene and acetylene clusters. The detailed estimation procedure of the ΔCCSD(T)(limit) is shown elsewhere.[S13]

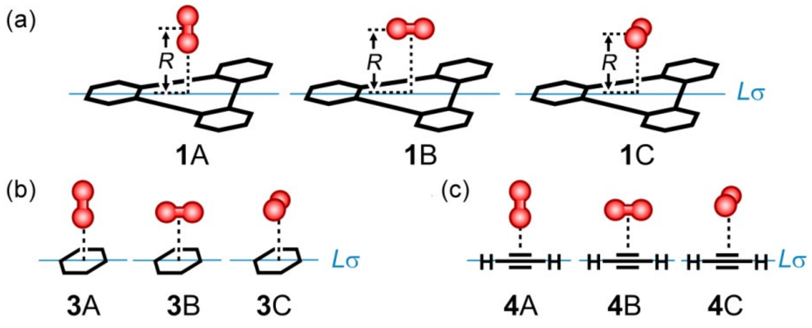

Fig. S1 Clusters of π molecules and a gas molecule: (a) **1** (b) **3,** and (c) **4** with (A) T-shaped, (B) parallel, and (C) twisted arrangements. In the T-shaped, the linear gas molecule is orthogonally stood up on the center of the π systems. In the parallel and twisted, the molecular axis of the gas is parallel and orthogonal to the *L*σ axis, respectively, where the *L*σ axis denotes the C_2 axis in **1**, the diagonal axis in **3**, and the molecular axis in **4**. *R* denotes the distance between center of the gas molecule and the π molecule.

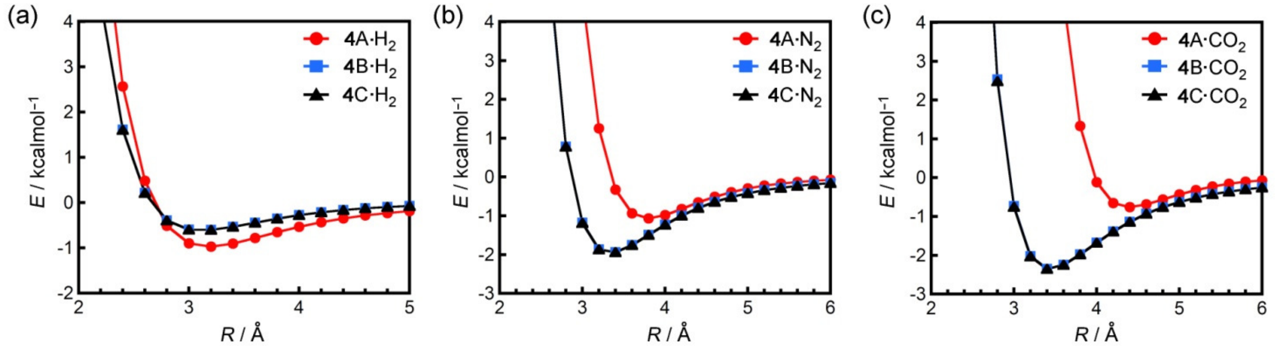

Fig. S2 Intermolecular interaction potentials calculated at the MP2/aug-cc-pVDZ level for benzene **3** clusters with (a) hydrogen, (b) nitrogen, and (c) carbon dioxide, where the orientations A, B, and C are denoted by red circle, blue square, and black triangle, respectively.

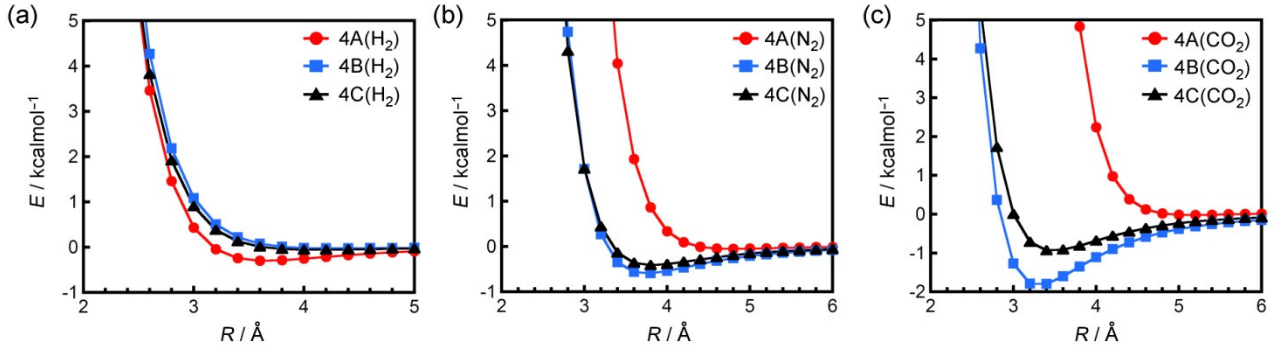

Fig. S3 Intermolecular interaction potentials calculated at the MP2/aug-cc-pVDZ level for acetylene **4** clusters with (a) hydrogen, (b) nitrogen, and (c) carbon dioxide, where the orientations A, B, and C are denoted by red circle, blue square, and black triangle, respectively.

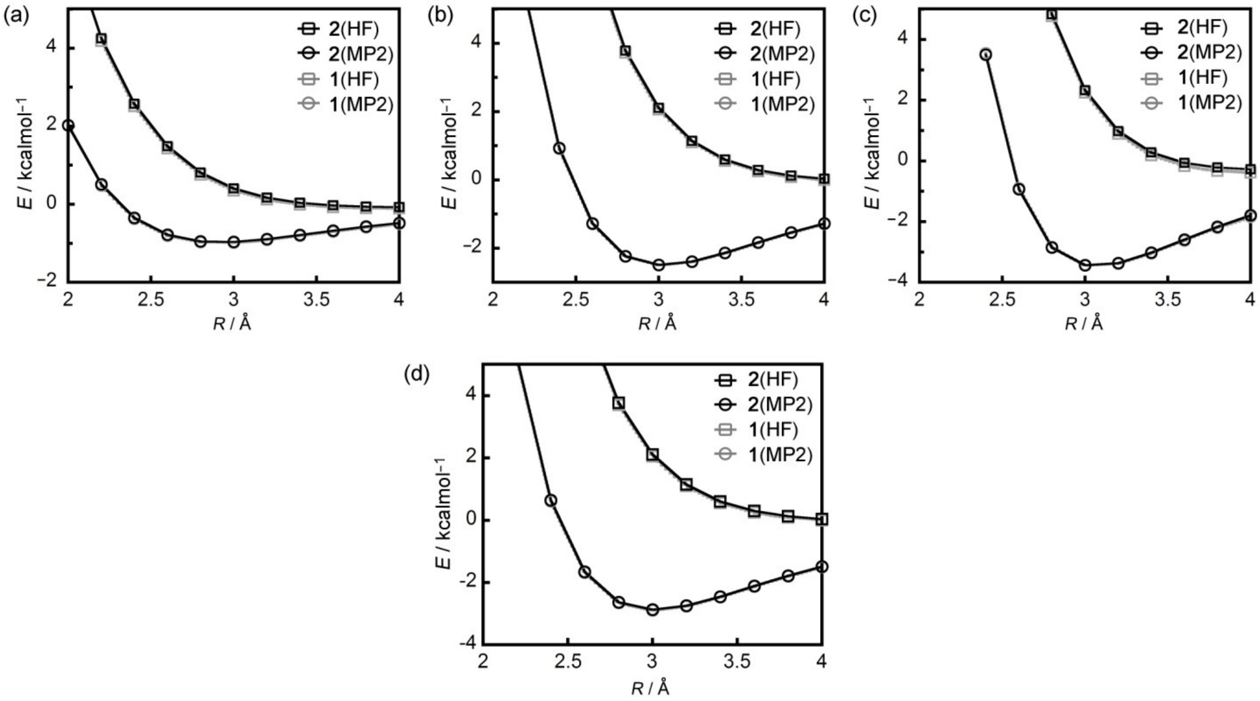

Fig. S4 Intermolecular interaction potentials calculated for clusters of DBAs **2** and **1** with gases by the HF (open square) and MP2 (open circle) methods with the cc-pVTZ basis set. (a) **2**A·H_2 in black and **1**A·H_2 in gray, (b) **2**B·N_2 in black and **1**B·N_2 in gray, and (c) **2**C·CO_2 in black and **1**C·CO_2 in gray. (d) The potentials of **2**B·N_2 and **1**B·N_2 calculated at aug-cc-pVDT level. The potentials (a)–(d) indicate that introduction of carboxy groups in the DBA core gives no influence on the interaction of the central pocket of the DBA with gas molecules.

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S10. The errors of the estimated interaction energies at the basis set limit associated with the extrapolation will be very small. The MP2 interaction energies calculated for the DBA-H_2 cluster (**1A**) at the potential minimum using the aug-cc-pVDZ and aug-cc-pVTZ basis sets are −1.094 and −1.244 kcal/mol, respectively. The estimated interaction energy at the basis set limit is −1.307 kcal/mol, which is very close to the MP2 level interaction energy calculated using the aug-cc-pVTZ basis set. The difference is 0.063 kcal/mol. The very small difference shows that the aug-cc-pVTZ basis set is nearly saturated, which suggests that the errors associated with the extrapolation are very small.

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