# SUPPORTING INFORMATION

# Methane Adsorption on Heteroatom-Modified Maquettes of Porous Carbon Surfaces

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**Figure S1.** Graphical illustrations of the nomenclature employed for adsorbent reference orientation and atom numbering. The central position 1 is the site of substitution (X1 position, X = C, B, or N). Relative to X1, the nearest neighbors (α positions) are numbered 2–4, the second-nearest neighbors (β positions) are numbered 5–10, and the third-nearest neighbors (γ positions) are numbered 11–13. The methylidene group carbon is numbered 14. While this is different from the IUPAC numbering convention, it is suited for clarity within the present work. The rings of the MPh models are labeled with roman numerals. Ring I contains the dangling methylidene group, which breaks the symmetry of the model. Rings II and III are adjacent and opposite to ring I, respectively.
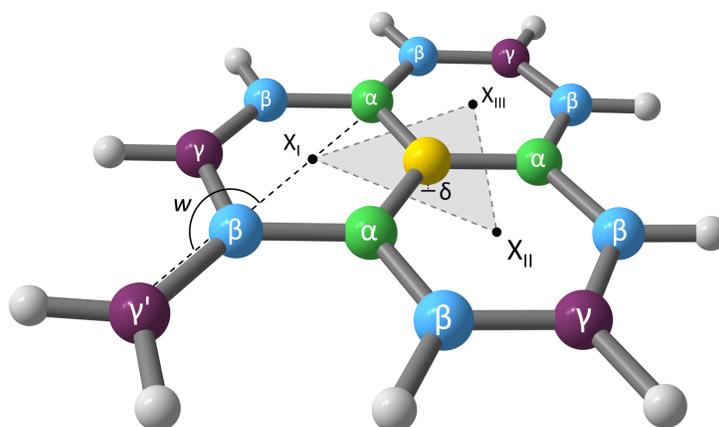


**Figure S2.** Graphical illustrations of the nomenclature employed for representative internal coordinates of the adsorbent. The "inner sphere" coordinates are defined by three C–C distances between the site of substitution (X1) and each of the αC atoms. The "outer sphere" is defined by six C–C distances between adjacent αC and βC atoms. The "peripheral sphere" is defined by six plus one C–C distances between adjacent βC and γC atoms, and the methylidene γ'C atom. The planarity of the molecule is described by the distance (δ) between the site of substitution (X1) and the plane formed by the ring centroids ($X_I$, $X_{II}$, and $X_{III}$). Finally, the out-of-plane wagging character of the methylidene group is defined by the angle (w) between the γ'C···*ipso*-βC···*para*-αC of ring I. Notably, the in-plane bending of the MPh structure is typically negligible owing to the extensive π-conjugation of all carbon/heteroatom sites.
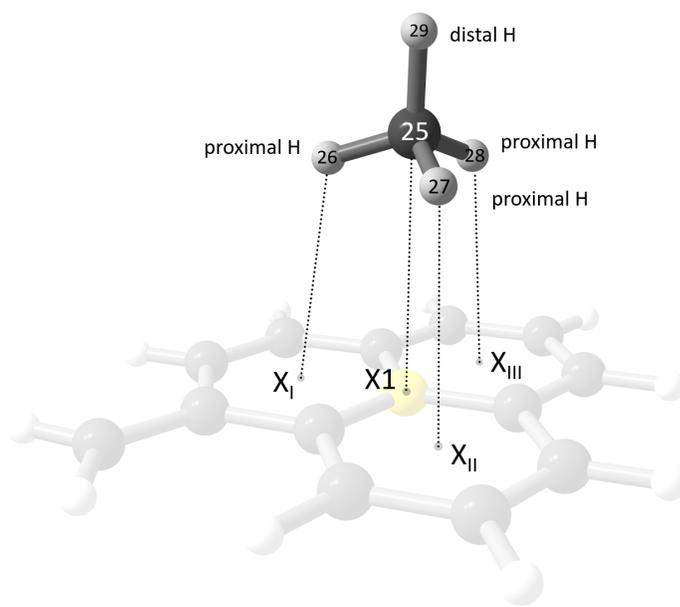
**Figure S3.** Graphical illustrations of the nomenclature employed for adsorption model geometry, atom numbering, and internal coordinates. The bond length of the adsorption interaction is defined by the distance between the methane carbon (C25) and site of substitution (X1), as well as the three distances between the proximal H atoms of the methane molecule and the nearest ring centroids (H26···$X_I$, H27···$X_{II}$, and H28···$X_{III}$). The distortion imposed by the adsorption interaction is defined by four C–H distances within the methane (adsorbate) molecule, and the dihedral angles ($\omega_I$, $\omega_{II}$, and $\omega_{III}$) between the methane C–H bonds and the closest ring centroid: C25–H(26,27,28)···X1···$\gamma$C(11,12,13). The C–H distances are further classified as proximal (C25–H26, C25–H27, and C25–H28) or distal (C25–H29) relative to the adsorbent surface.
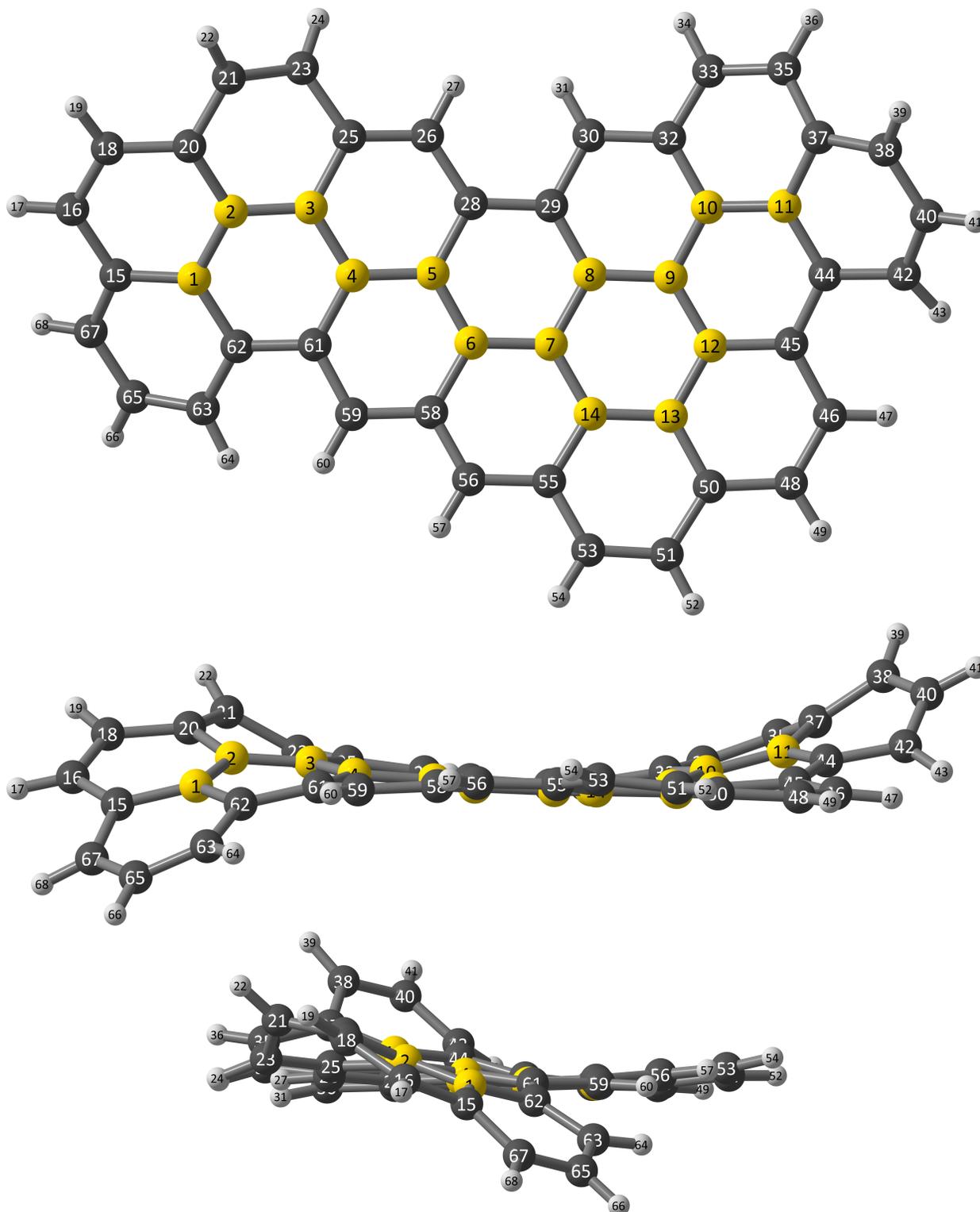
**Figure S4.** Top and side views of a larger "curved blade" *maquette* ($XC_{47}H_{20}$) with fourteen possible sites of substitution (X = C, B, or N) for $CH_4$ adsorption, shown in yellow. Only one of the fourteen sites is substituted with B or N in each calculation, the remainder remaining as C.
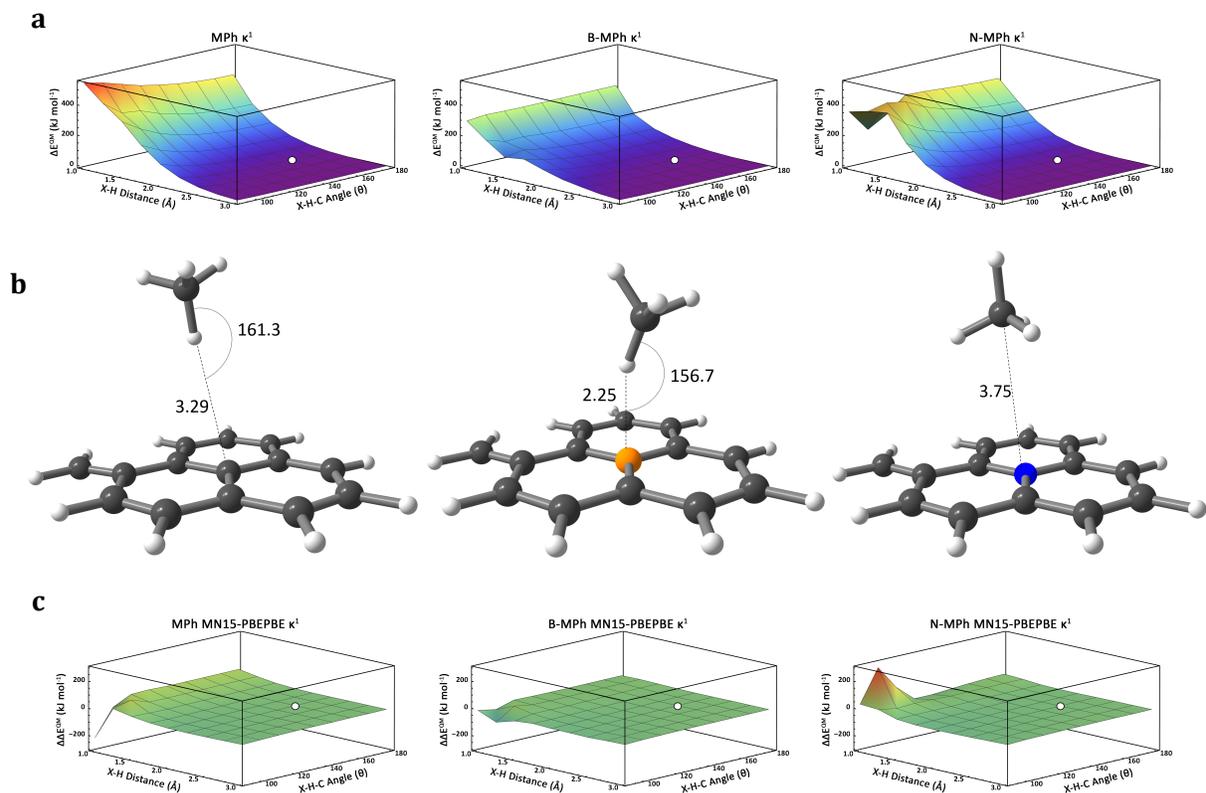
**Figure S5.** (a) Potential energy surface maps for methane interactions with MPh and its heteroatom-substituted variants (B-MPh and N-MPh) in $\kappa^1$ approach geometry at the PBE/6-311++G** level. (b) The PBE optimized adsorption models MPh×CH$_4$, B-MPh×CH$_4$, and N-MPh×CH$_4$ in their starting geometries used for structural optimizations. (c) Potential energy difference maps between the PBE/6-311++G** and the MN15/6-311++G** levels of theory.
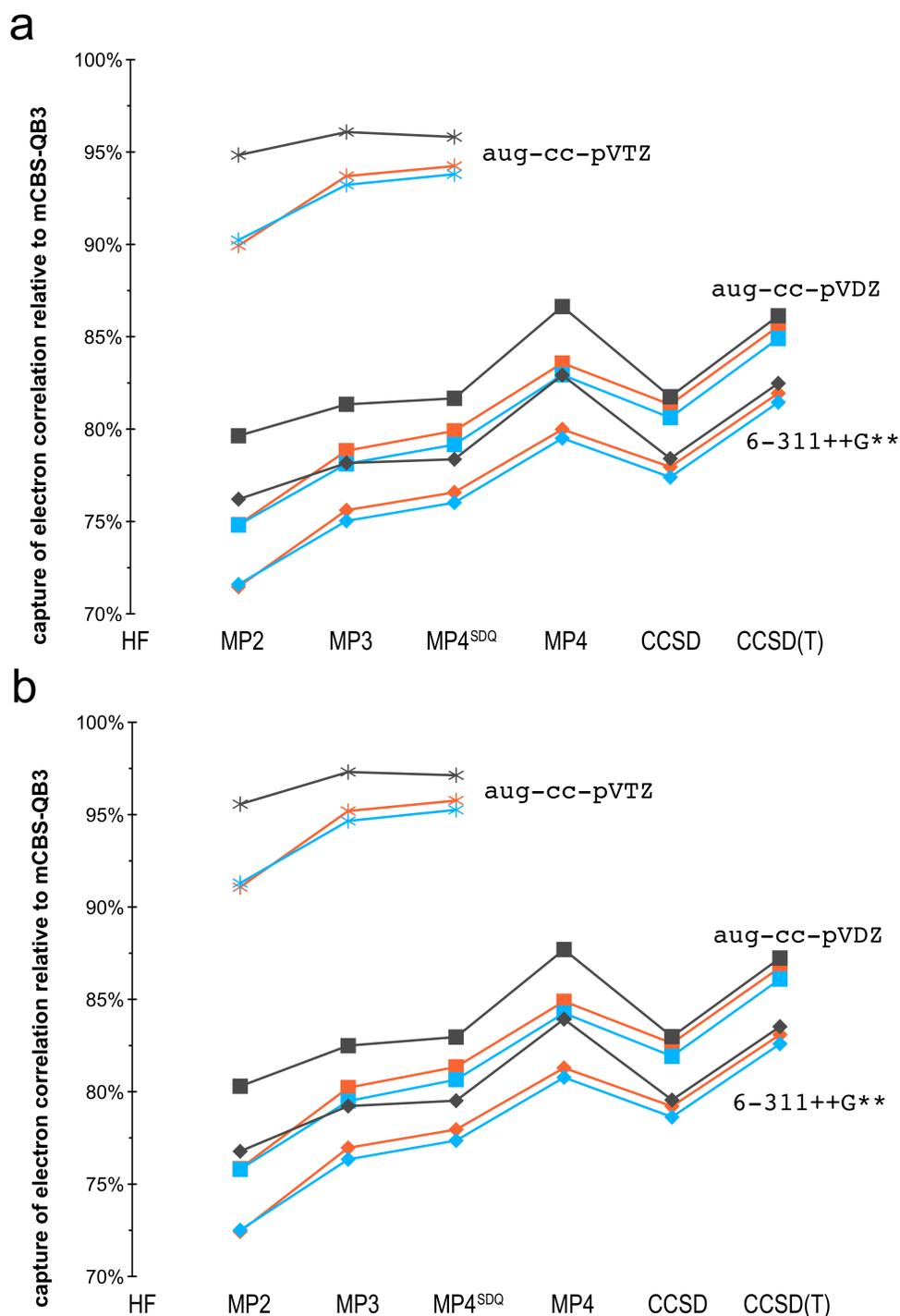
**Figure S6.** Comparison of the completeness of capturing electron correlation with the employed levels of correlated MO theory as a function of 6-311++G** (diamond), *aug-cc*-pVDZ (square), and *aug-cc*-pVTZ (star) basis sets for MPh (gray), B-MPh (orange) and N-MPh (light blue), for (a) the adsorbent models and (b) the adsorption models. The 1.2±0.2% shift between the two sets of curves and the identical trends (parallel lines within 2% variation) between the results with and without the triples substitution (T) allows for the extrapolation of the missing CCSD and CCSD(T) results for the *aug-cc*-pVTZ basis set.
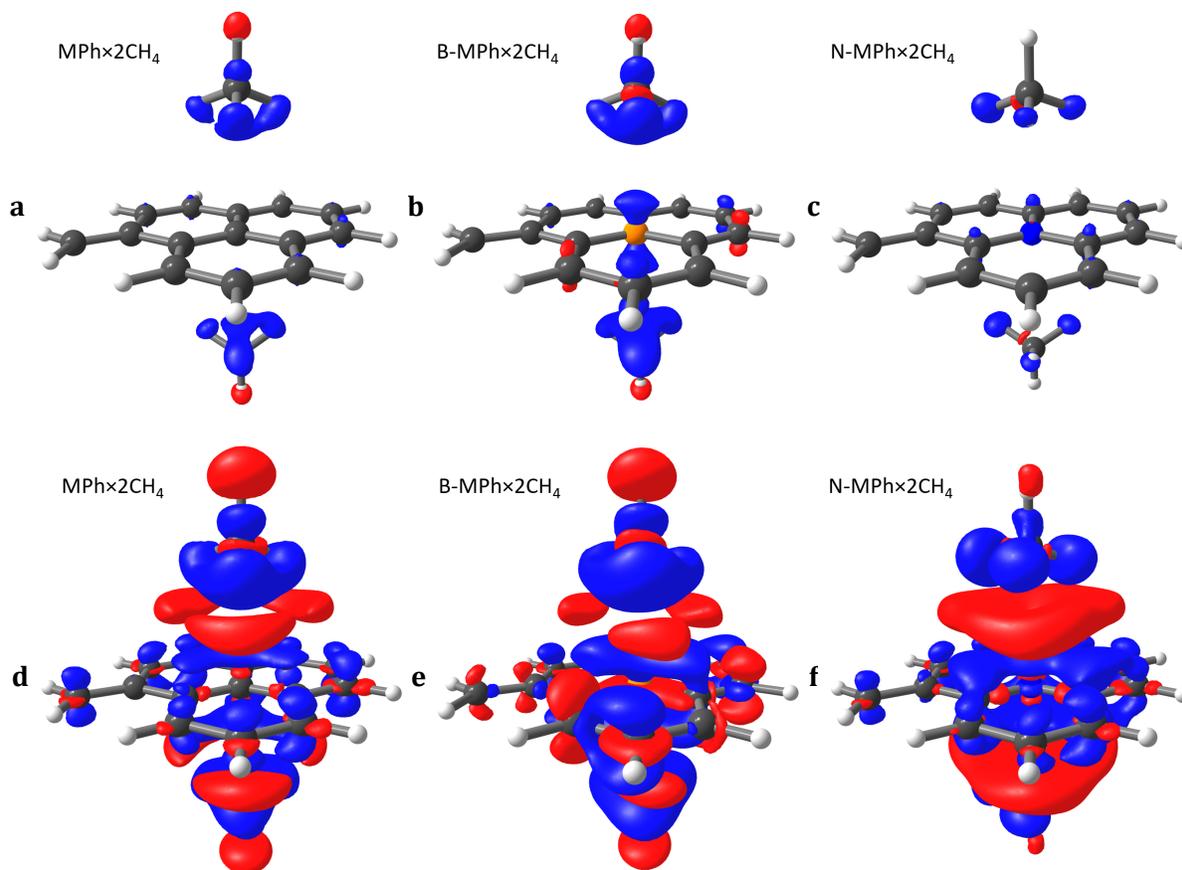
**Figure _S7._** Electron density difference plots for methane interactions with MPh and its heteroatom-substituted variants: (a-c) at a high contour level of $5\times10^{-4}$ $(e^-)^2$ Å$^{-3}$ and (d-f) at a low contour level of $1.5\times10^{-4}$ $(e^-)^2$ Å$^{-3}$ for MPh×2CH$_4$ (a,d), B-MPh×2CH$_4$ (b,e), and N-MPh×2CH$_4$ (c,f). Electron density difference between the double adsorption model and the separate adsorbent and adsorbates at the MN15/def2-QZVPP level is shown (positive difference in red, negative difference in blue). See **Figure 3** for the corresponding single (n = 1) adsorption models.
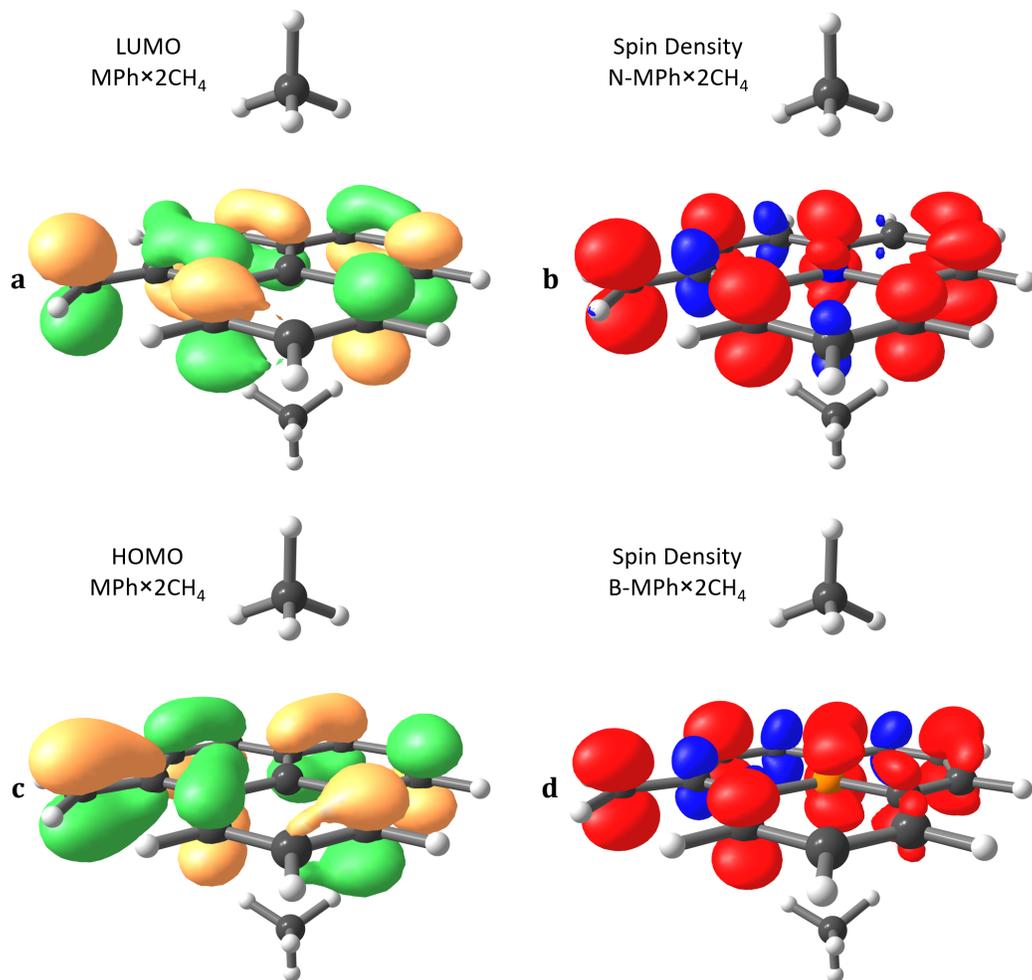
**Figure S8.** Comparison of the electron density of MPh and the spin density of B-MPh and N-MPh upon methane adsorption. (a) LUMO and (c) HOMO electron density contour plots for MPh×2CH$_4$ at a contour level of $4.5 \times 10^{-2}$ ($e^-$)$^2$ Å$^{-3}$ and (b,d) spin density contour plots for N-MPh×2CH$_4$ and B-MPh×2CH$_4$ at a contour level of $3.5 \times 10^{-3}$ ($e^-$)$^2$ Å$^{-3}$. See **Figure 4** for the corresponding single (n = 1) adsorption models.
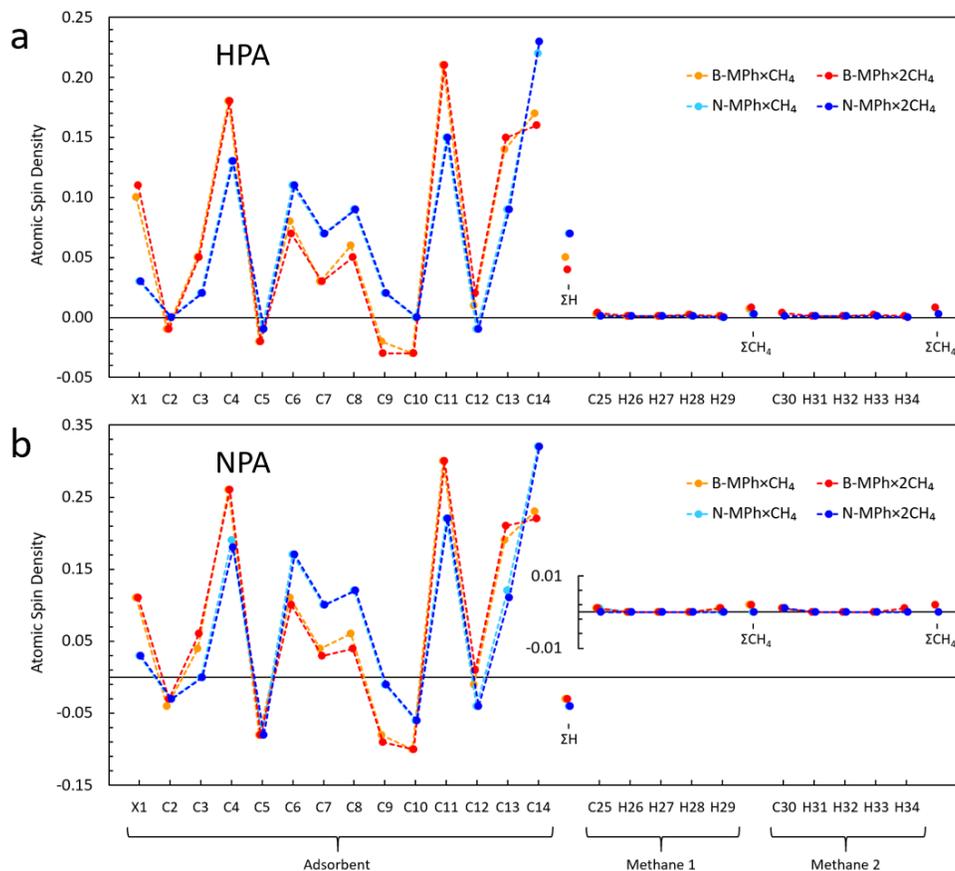
**Figure S9.** Atomic spin density distribution analysis upon single (n = 1) and double (n = 2) methane adsorption on B-MPh (orange/red) and N-MPh (cyan/blue) determined by two conceptually different population analysis methods: (a) Hirshfeld (HPA) and (b) Weinhold (NPA), at the MN15/def2-QZVPP level of theory. See **Figures S1-S3** for the atomic numbering and **Tables S11–S12** for the tabulated data.

The unpaired electron distribution among the atomic constituents of the MPh×nCH$_4$ adsorption models at the MN15+ level, as calculated by the HPA and NPA analysis methods, is shown in **Figure S8** (see also **Tables S9–S10**). Contrary to the variations in atomic charges that are the sum of spin-up ($\alpha$) and spin-down ($\beta$) one-electron densities (wherein errors accumulate), the spin densities show only negligible dependence on the population analysis method (due to error cancelation). The Weinhold analysis (NPA) displays a slightly larger spin polarization than the Hirshfeld analysis (HPA); however, the overall spin density distribution as a function of atom location in the adsorption system is identical in both cases. The different compositions of the spin-up and spin-down orbitals, and thus the multi-reference nature of the wave function, are demonstrated by the presence of both positively and negatively signed atomic spin densities in an ordered and characteristic manner, independent of the identity of substitution. While the atomic charge distribution undulates (**Figure 2** and **Tables S9-S10**) as a function of distance from the site of substitution (X1), the atomic spin densities show the opposite trend as the peripheral ($\gamma$) atoms accumulate the largest spin density. Exploratory calculations using larger, extended *maquette*

molecules (results not shown) confirm that the extra electron/electron hole delocalizes to the periphery of the conjugated polycyclic molecule and does not stay localized to the inner or outer sphere of the site of substitution as the origin of spin polarization. Hirshfeld analysis (HPA) shows to a greater extent than Weinhold analysis (NPA) that the methane adsorbate also undergoes a slight spin polarization: 0.008 e$^-$ for B-MPh×nCH$_4$ and 0.003 e$^-$ N-MPh×nCH$_4$ (**Figure 5** and **Table S12**). This is a direct indication of the presence of a small, but non-negligible magnetic interaction between the adsorbate and adsorbent in addition to the above discussed induced ionic interactions due to mutual polarization of the constituents of the adsorption system.

To a modest degree, the spin polarization also appears in the expectation value of the spin operator $<S^2>$ at the MN15+ level. The $<S^2>$ values are 0.791 and 0.783 for B-MPh×nCH$_4$ and N-MPh×nCH$_4$, respectively. Upon spin annihilation by eliminating contributions from the $M_s$ = ½ sublevel of the higher S = $^3/_2$ spin state, the $<S^2>$ values for both systems are reduced to 0.751, which is close to the ideal, non-contaminated expectation value of S(S+1) = 0.750. The reference wave function level for correlated MO calculations (HF/6-311++G**) shows a dramatically larger deviation from the ideal value (2.486 and 2.448). This result becomes even greater (4.982 and 4.725) upon spin annihilation, indicating significant contributions of the $M_s$ = ½ sublevel of the S = $^5/_2$ and likely higher spin states. Deviations from the ideal spin expectation value can be mitigated by constructing a restricted open-shell (ROHF) S = ½ electronic structure calculation; however, this wave function corresponds to a significantly higher energy state by +173 and +158 kJ mol$^{-1}$ for the B-MPh×CH$_4$ and N-MPh×CH$_4$ models, respectively. These large energy values are indicative of the significant static electron correlation as captured by allowing for different composition of spin-up and spin-down one-electron orbitals in the unrestricted (UHF) calculation. Analogously, the use of the spin-polarized B-MPh×CH$_4$ and N-MPh×CH$_4$ electronic structures as initial wave functions results in a spin-unrestricted, open-shell singlet electronic structure for the unsubstituted MPh×CH$_4$ *maquette* at a lower energy structure (-110 kJ mol$^{-1}$) than the closed-shell, diamagnetic state, at the restricted HF/6-311++G** level. The energy differences between the spin-polarized (UHF) and spin-restricted (ROHF) electronic structures are gradually diminished as more complete treatment of electron correlation is employed: 264-287 at MP2, 138-152 at MP3, 98-112 at MP4$^{SDQ}$, 19-30 at CCSD, and finally 43-47 at CCSD(T), in kJ mol$^{-1}$. The complexity of the spin manifold also explains the computational challenges of obtaining equilibrium structures that were burdened by chronic oscillations in SCF cycles, jumping arbitrarily to higher energy potential energy surfaces that correspond to resonance structures with non-planar, puckered geometries. Further multi-reference CASSCF/CASMP2 calculations are warranted in order to obtain a complete, detailed picture of methane interactions with MPh-based molecular *maquettes* of carbon surfaces, but remain relegated to future work.
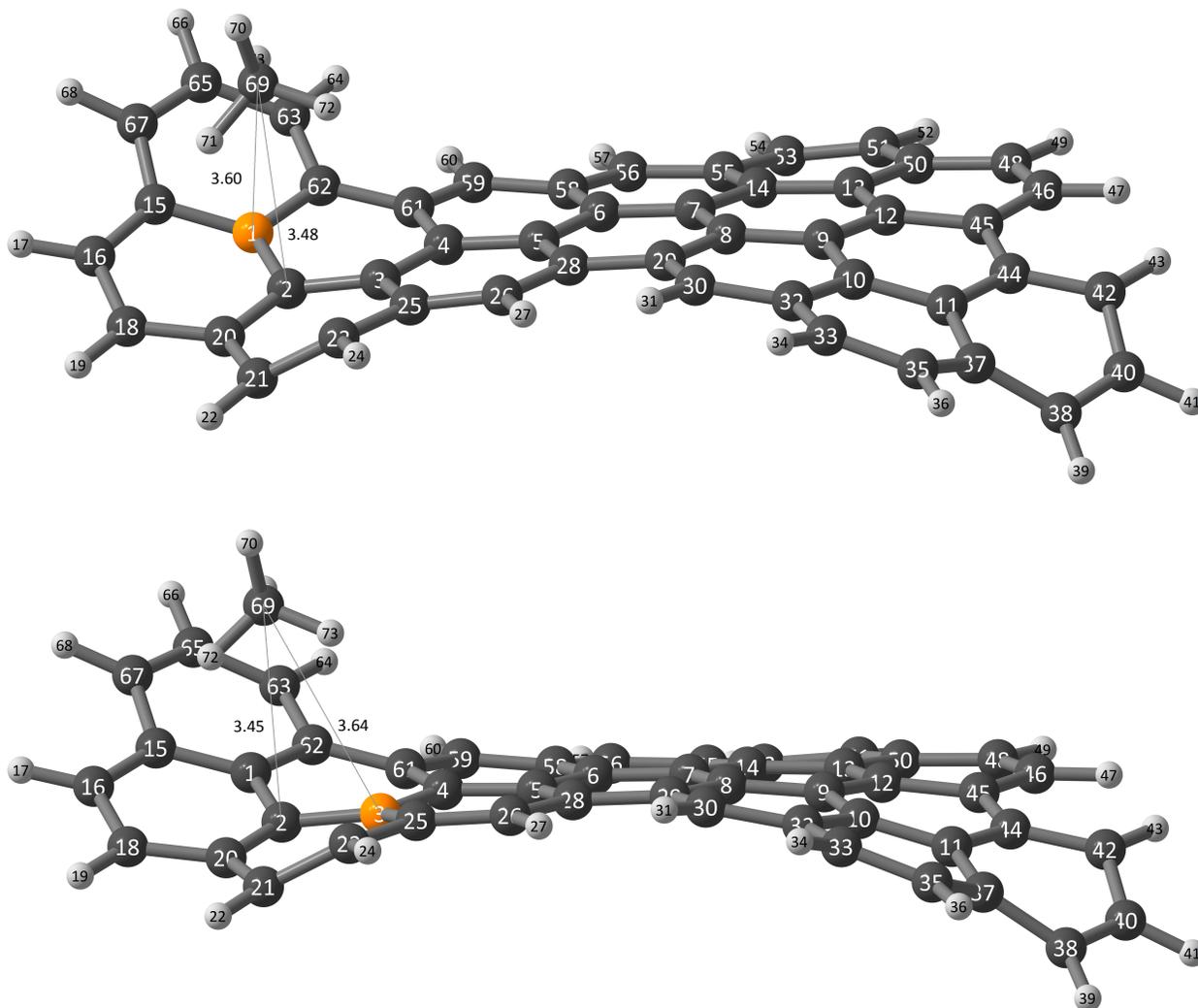
**Figure S10.** Stationary structures of the two "curved blade" adsorption models ($BC_{47}H_{20}$), where the $CH_4$ adsorbate slipped to an adjacent adsorption site due to the curvature and distortion of the aromatic π-system. Optimization was performed at the MN15/6-31G* (MN15−) level.

**Table S1:** Overview of literature examples of experimental (top) and theoretical (bottom) investigations of methane adsorption on carbon surfaces. The sign convention corresponds to energy of dissociation/desorption. All experimental and theoretical values refer to isosteric heat of desorption ($q_{st}$) from gas adsorption measurements and calculated desorption energy ($\Delta_{des}E$) from quantum potential energy differences, respectively.

*Experimental Studies:*

| Author(s) | Year | DOI | Adsorbent | | Method | $q_{st}$, kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Chahine | 1997 | 10.1021/la960843x | activated carbon | CNS-201 | Gas adsorption | |
| Salem | 1998 | 10.1021/la970119u | activated carbon | AS activated carbon | Gas adsorption | 14.35 |
| Lozano-Castelló | 2002 | 10.1016/S0008-6223(02)00194-X | activated carbon | KOH-activated anthracite-based | Gas adsorption | |
| Zhou | 2007 | 10.1021/jp074889i | MOFs | MOF5 and ZIF8 | Gas adsorption | ~12.2 |
| Stadie | 2013 | 10.1021/ja311415m | microporous carbons | ZTC, MSC-30, CNS-201 | Gas adsorption | 13.5…19.5 |
| Yuan | 2013 | 10.1021/es4000643 | ordered mesoporous carbon | soft templated ordered mesoporous carbon (sOMC) | Gas adsorption | 15.4 |
| Stadie | 2015 | 10.1021/acs.jpcc.5b05021 | microporous carbons | ZTC, MSC-30, CNS-201 | Gas adsorption | ~14, 15, 19 |
| Kim | 2018 | 10.1016/j.micromeso.2018.06.021 | N-doped | nitrogen-doped crab shell-derived carbon nanofibers | Gas adsorption | 18.9…20.7 |

*Theoretical Studies:*

| Author(s) | Year | DOI | Adsorbent | | | Theory | $\Delta_{des}E$ ,kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Matranga | 1992 | 10.1016/0009-2509(92)85005-V | activated carbon | carbon slit pore | | GCMC, isosteric | ~12 [a] |
| Cracknell | 1993 | 10.1021/j100104a036 | microporous carbon | carbon slit pore | | GCMC, isosteric | ~12 [a] |
| Bhatia | 2006 | 10.1021/la0523816 | porous carbon | carbon slit pore | | GCMC, isosteric | 16 |
| Palmer | 2009 | 10.1016/j.carbon.2009.06.037 | coal-based activated carbon | hybrid reverse MC-derived amorphous microporous carbon | | GCMC, isosteric | ~19[a] |
| Smith | 2012 | 10.1021/ct3008809 | polyaromatic hydrocarbons | open surface | | CCSD(T)+MP2 | ~14…~20 |
| Lui | 2013 | 10.1016/j.apsusc.2013.08.035 | graphene | open surface | | DFT (LDA CA-PZ) | 9.8…14.9 |
| Chen | 2015 | 10.1109/LED.2015.2492580 | monolayer and multilayer graphene | open surface | | DFT (LDA GGA) | 43.4 |
| Hussain | 2015 | 10.1002/jcc.24242 | buckybowls | open surface | | DFT (M05-2X) | 4.6…20.3 |
| | | | coronene | open surface | | DFT (M05-2X) | 4.6…20.3 |
| Burrill | 2020 | 10.1039/D0CP02645J | buckybowls | open surface | | DFT (ωB97M-V/pc-2) | 7.23…23.3 |
| Denis | 2008 | 10.1016/j.chemphys.2008.07.024 | N-doped | nanotube segments | curved surface | DFT (LDA) | 10.3…31.0 |
| Lui | 2013 | 10.1016/j.apsusc.2013.08.035 | B-doped | graphene | open surface | DFT (LDA CA-PZ) | 6.2…14.8 |
| | | | N-doped | graphene | open surface | DFT (LDA CA-PZ) | 2.9…17.3 |
| Wang | 2015 | 10.1002/pssb.201451632 | N-doped | graphene | open surface | DFT (PBE) | 10.6…206.5 |
| Chen | 2015 | 10.1109/LED.2015.2492580 | B-doped | monolayer and multilayer graphene | open surface | DFT (LDA GGA) | 49.2 |
| | | | N-doped | monolayer and multilayer graphene | open surface | DFT (LDA GGA) | 41.5 |
| Hassani | 2016 | 10.1016/j.comptc.2016.02.019 | B-doped | graphene | open surface | DFT D3 | 7.5…17.5 |
| | | | N-doped | graphene | open surface | DFT D3 | 5.4…13.4 |

[a] isosteric heat value.

**Table S2.** Graphical illustration and Z-matrix definitions for κ¹, μ₂, μ₃, and η² approaches of CH₄ to the X1 position of MPh and its heteroatom substituted variants.

| κ¹ CH₄ bonding | μ₂ CH₄ bonding | μ₃ CH₄/tetrel bonding | η²(C–H) CH₄ bonding |
|---|---|---|---|



| κ¹ CH₄ bonding | μ₂ CH₄ bonding | μ₃ CH₄/tetrel bonding | η²(C–H) CH₄ bonding |
|---|---|---|---|
| B/C/N | B/C/N | B/C/N | B/C/N |
| H 1 rCH | X 1 rCX | X 1 rCX | C |
| X 2 1.0   1 90.0 | X 2 rXX 1 qXXC | X 2 rXX 1 qXXC | X 1 rCX |
| C 2 rCHm  3 qCHX  1  wCHXC | C 2 rCX 3 qCXX 1 wCXXC | C 2 rCX 3 qCXX 1 wCXXC | H 2 rHX 1 qHXC |
| H 4 rCHm  2 qHCH  3 -wHaCHX | H 4 rHC 3 qHCX 1 wHCXC | H 4 rHC 2 qHCX 3 wHCXX | C 3 rCH 2 qCHX 1 wCHXC |
| H 4 rCHm  2 qHCH  3 wHbCHX | H 4 rHC 5 qHCH 1 wHaCHC | H 4 rHC 5 qHCH 3 wHaCHX | H 4 rHC 3 qHCH 1 -wHaCHC |
| H 4 rCHm  2 qHCH  3 wHaCHX | H 4 rHC 5 qHCH 1 -wHbCHC | H 4 rHC 5 qHCH 3 wHbCHX | H 4 rHC 3 qHCH 1 wHbCHC |
| C 1 rCaC  2 qCaCH  3 wCaaCHX | H 4 rHC 5 qHCH 1 wHcCHC | H 4 rHC 5 qHCH 3 -wHbCHX | H 4 rHC 3 qHCH 1 wHaCHC |
| C 1 rCaC  2 qCaCH  3 wCabCHX | C 1 rCaC 2 qCaCX 3 wCaaCXX | C 1 rCaC 2 qCaCX 3 wCaaCXX | C 1 rCaC 2 qCaCX 4 wCaaCXC |
| C 1 rCaC  2 qCaCH  3 -wCabCHX | C 1 rCaC 2 qCaCX 3 -wCaaCXX | C 1 rCaC 2 qCaCX 3 -wCaaCXX | C 1 rCaC 2 qCaCX 4 -wCabCXC |
| C 8 rCbCa  1 qCbCaC 2 -wCbCaCH | C 1 rCaC 2 qCaCX 3 wCabCXX | C 1 rCaC 2 qCaCX 3 wCabCXX | C 1 rCaC 2 qCaCX 4 wCabCXC |
| C 8 rCbCa  1 qCbCaC 2 wCbCaCH | C 9 rCbCa 1 qCbCaC 2 -wCbCaCX | C 9 rCbCa 1 qCbCaC 2 -wCbCaCX | C 8 rCbCa  1 qCbCaC 2 -wCbCaCX |
| C 9 rCbCa  1 qCbCaC 2 wCbCaCH | C 9 rCbCa 1 qCbCaC 2 wCbCaCX | C 9 rCbCa 1 qCbCaC 2 wCbCaCX | C 8 rCbCa  1 qCbCaC 2 wCbCaCX |
| C 9 rCbCa  1 qCbCaC 2 -wCbCaCH | C 10 rCbCa 1 qCbCaC 2 wCbCaCX | C 10 rCbCa 1 qCbCaC 2 wCbCaCX | C 9 rCbCa  1 qCbCaC 2 wCbCaCX |
| C 10 rCbCa  1 qCbCaC 2 wCbCaCH | C 10 rCbCa 1 qCbCaC 2 -wCbCaCX | C 10 rCbCa 1 qCbCaC 2 -wCbCaCX | C 9 rCbCa  1 qCbCaC 2 -wCbCaCX |
| C 10 rCbCa  1 qCbCaC 2 -wCbCaCH | C 11 rCbCa 1 qCbCaC 2 wCbCaCX | C 11 rCbCa 1 qCbCaC 2 wCbCaCX | C 10 rCbCa  1 qCbCaC 2 wCbCaCX |
| C 11 rCmCb 8 qCmCbCa 1 wCmCbCaC | C 11 rCbCa 1 qCbCaC 2 wCbCaCX | C 11 rCbCa 1 qCbCaC 2 wCbCaCX | C 10 rCbCa  1 qCbCaC 2 -wCbCaCX |
| H 17 rHCm  11 qHCmCb 8 wHCmCbCa | C 12 rCmCb 9 qCmCbCa 1 wCmCbCaC | C 12 rCmCb 9 qCmCbCa 1 wCmCbCaC | C 11 rCmCb 8 qCmCbCa 1 wCmCbCaC |
| H 17 rHCm  11 qHCmCb 8 wHCmCbH | H 18 rHCm 12 qHCmCb 9 wHCmCbCa | H 18 rHCm 12 qHCmCb 9 wHCmCbCa | H 17 rHCm  11 qHCmCb 8 wHCmCbCa |
| C 11 rCcCb 8 qCcCbCa 1 wCcCbCaC | H 18 rHCm 12 qHCmCb 19 wHCmCbH | H 18 rHCm 12 qHCmCb 19 wHCmCbH | H 17 rHCm  11 qHCmCb 8 wHCmCbH |
| H 20 rHC  11 qHCcCb 8 wHCcCbCa | C 12 rCcCb 9 qCcCbCa 1 wCcCbCaC | C 12 rCcCb 9 qCcCbCa 1 wCcCbCaC | C 11 rCcCb 8 qCcCbCa  1 wCcCbCaC |
| C 12 rCcCb 8 qCcCbCa 1 wCcCbCaC | H 21 rHCc 12 qHCcCb 9 wHCcCbCa | H 21 rHCc 12 qHCcCb 9 wHCcCbCa | H 20 rHC  11 qHCcCb 8 wHCcCbCa |
| H 22 rHC  11 qHCcCb 8 wHCcCbCa | C 13 rCcCb 9 qCcCbCa 1 wCcCbCaC | C 13 rCcCb 9 qCcCbCa 1 wCcCbCaC | C 12 rCcCb 8 qCcCbCa 1 wCcCbCaC |
| C 14 rCcCb 9 qCcCbCa 1 wCcCbCaC | H 23 rHCc 13 qHCcCb 9 wHCcCbCa | H 23 rHCc 13 qHCcCb 9 wHCcCbCa | H 22 rHC  11 qHCcCb 8 wHCcCbCa |
| H 24 rHC  14 qHCcCb 9 wHCcCbCa | C 15 rCcCb 10 qCcCbCa 1 wCcCbCaC | C 15 rCcCb 10 qCcCbCa 1 wCcCbCaC | C 14 rCcCb 9 qCcCbCa 1 wCcCbCaC |
| H 12 rHC  8 qHCbCa  1 qHCbCaC | H 25 rHCc 15 qHCcCb 10 wHCcCbCa | H 25 rHCc 15 qHCcCb 10 wHCcCbCa | H 24 rHC  14 qHCcCb 9 wHCcCbCa |
| H 13 rHC  9 qHCbCa  1 qHCbCaC | H 13 rHCb 9 qHCbCa 1 wHCbCaC | H 13 rHCb 9 qHCbCa 1 wHCbCaC | H 12 rHC  8 qHCbCa  1 qHCbCaC |
| H 14 rHC  9 qHCbCa  1 qHCbCaC | H 14 rHCb 10 qHCbCa 1 wHCbCaC | H 14 rHCb 10 qHCbCa 1 wHCbCaC | H 13 rHC  9 qHCbCa  1 qHCbCaC |
| H 15 rHC  10 qHCbCa  1 qHCbCaC | H 15 rHCb 10 qHCbCa 1 wHCbCaC | H 15 rHCb 10 qHCbCa 1 wHCbCaC | H 14 rHC  9 qHCbCa  1 qHCbCaC |
| H 16 rHC  10 qHCbCa  1 qHCbCaC | H 16 rHCb 11 qHCbCa 1 wHCbCaC | H 16 rHCb 11 qHCbCa 1 wHCbCaC | H 15 rHC  10 qHCbCa  1 qHCbCaC |
|  | H 17 rHCb 11 qHCbCa 1 wHCbCaC | H 17 rHCb 11 qHCbCa 1 wHCbCaC | H 16 rHC  10 qHCbCa  1 qHCbCaC |
|  |  |  |  |
| rCH 3.0 8 -0.25 | rCX 2.5 8 -0.25 | rCX 2.5 8 -0.25 | rCX 3.0 8 -0.25 |
| rCHm 1.09 | rXX 1.0 | rXX 1.0 | rHX 0.545 |
| qCHX 88.9 8 -11.1 | qXXC 90.0 | qXXC 90.0 | qHX 89.9 8 -11.1 |
| wCHXC 180.0 | rCX 0.5 | rCX 0.5 | rCH 1.09 |
| qHCH 120.0 | qCXX 90.0 | qCXX 90.0 | qCHX 0.0 |
| wHaCHX 60.0 | wCXXC 180.0 | wCXXC 180.0 | wCHXC 90.0 |
| wHbCHX 180.0 | rHC 1.09 | rHC 1.09 | rHC 1.09 |
| rCaC 1.435 | qHCX 178.9 6 -11.1 | qHCX 178.9 6 -11.1 | qHCH 109.5 |
| qCaCH 90.0 | wHCXC 0.0 | wHCXX 90.0 | wHaCHC 60.0 |
| wCaaCHX 180.0 | wHaCHC 0.0 | qHCH 109.5 | wHbCHC 180.0 |
| wCabCHX 60.0 | wHbCHC 120.0 | wHaCHX 180.0 | rCaC 1.435 |
| rCbCa 1.435 | wHcCHC 120.0 | wHbCHX 60.0 | qCaCX 90.0 |
| qCbCaC 120.0 | qHCH 109.5 | rCaC 1.435 | wCaaCXC 0.0 |
| wCbCaCH 90.0 | rCaC 1.435 | qCaCX 90.0 | wCabCXC 120.0 |
| rCmCb 1.36 | qCaCX 90.0 | wCaaCXX 60.0 | rCbCa 1.435 |
| qCmCbCa 120.0 | wCaaCXX 60.0 | wCabCXX 180.0 | qCbCaC 120.0 |
| wCmCbCaC 180.0 | wCabCXX 180.0 | rCbCa 1.435 | wCbCaCX 90.0 |
| rHCm 1.1 | rCbCa 1.435 | qCbCaC 120.0 | rCmCb 1.36 |
| qHCmCb 120.0 | qCbCaC 120.0 | wCbCaCX 90.0 | qCmCbCa 120.0 |
| wHCmCbCa 0.0 | wCbCaCX 90.0 | rCmCb 1.36 | wCmCbCaC 180.0 |
| wHCmCbH 180.0 | rCmCb 1.36 | qCmCbCa 120.0 | rHCm 1.1 |
| rCcCb 1.4 | qCmCbCa 120.0 | wCmCbCaC 180.0 | qHCmCb 120.0 |
| qCcCbCa 120.0 | wCmCbCaC 180.0 | rHCm 1.09 | wHCmCbCa 0.0 |
| wCcCbCaC 0.0 | rHCm 1.09 | qHCmCb 120.0 | wHCmCbH 180.0 |
| rHC 1.09 | qHCmCb 120.0 | wHCmCbCa 180.0 | rCcCb 1.4 |
| qHCcCb 120.0 | wHCmCbCa 180.0 | wHCmCbH 180.0 | qCcCbCa 120.0 |
| wHCcCbCa 180.0 | wHCmCbH 180.0 | rCcCb 1.435 | wCcCbCaC 0.0 |
| qHCbCa 120.0 | rCcCb 1.435 | qCcCbCa 120.0 | qHCcCb 120.0 |
| qHCbCaC 180.0 | qCcCbCa 120.0 | wCcCbCaC 0.0 | wHCcCbCa 180.0 |
|  | wCcCbCaC 0.0 | rHCc 1.09 | qHCbCa 120.0 |
|  | rHCc 1.09 | qHCcCb 120.0 | qHCbCaC 180.0 |
|  | qHCcCb 120.0 | wHCcCbCa 180.0 |  |
|  | wHCcCbCa 180.0 | rHCb 1.09 |  |
|  | rHCb 1.09 | qHCbCa 120.0 |  |
|  | qHCbCa 120.0 | wHCbCaC 180.0 |  |
|  | wHCbCaC 180.0 |  |  |

**Table S3.** Free adsorbent structures (LoT: MN15 using the STO-3G {MN15}, SDDAll [MN15], 6-31G* (MN15–),def2-QZVPP (MN15+), or *aug-cc*-pVTZ (MN15cc) basis sets) of MPh, B-MPh, and N-MPh as described by averages and standard deviations of inner, outer, and peripheral sphere C–C distances in Å, out-of-planarity ($\delta$, in Å) of the site of substitution, and wagging angle ($w$, in degrees) of the methylidene group (see **Table S4** for the geometry upon methane adsorption).

| Adsorbent | LoT | Inner, Å | Outer, Å | Peripheral, Å | $\delta$, Å | $w$, ° |
|---|---|---|---|---|---|---|
| MPh | {MN15} | 1.44±0.01 | 1.43±0.05 | 1.41±0.05 | 0.00 | 177 |
| | [MN15] | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.00 | 177 |
| | MN15– | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.00 | 176 |
| | MN15+ | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.00 | 176 |
| | MN15cc | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.00 | 176 |
| | | | | | | |
| B-MPh | {MN15} | 1.52±0.01 | 1.44±0.05 | 1.42±0.05 | 0.00 | 174 |
| | [MN15] | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.00 | 173 |
| | MN15– | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.00 | 172 |
| | MN15+ | 1.51±0.01 | 1.41±0.04 | 1.41±0.04 | 0.00 | 172 |
| | MN15cc | 1.51±0.01 | 1.41±0.04 | 1.41±0.04 | 0.00 | 172 |
| | | | | | | |
| N-MPh | {MN15} | 1.44±0.01 | 1.44±0.05 | 1.41±0.04 | 0.00 | 179 |
| | [MN15] | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15– | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.01 | 179 |
| | MN15+ | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15cc | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.00 | 179 |

**Table S4.** Adsorbent structures upon adsorption (LoT: MN15, MP2, MP4$^{SDQ}$, or CCSD using the 6-311++G** basis set, or MN15 using the STO-3G {MN15}, SDDAll [MN15], 6-31G* (MN15–), def2-QZVPP (MN15+), or *aug-cc*-pVTZ (MN15cc) basis sets) of methane on MPh, B-MPh, and N-MPh, as described by averages and standard deviations of inner, outer, and peripheral sphere C–C distances in Å, out-of-planarity (δ, in Å) of the site of substitution, and wagging angle (*w*, in degrees) of the methylidene group (see **Tables 1** and **S3** for the free adsorbent structures).

| Adsorbent | LoT | n | Inner, Å | Outer, Å | Peripheral, Å | δ, Å | *w*, ° |
|---|---|---|---|---|---|---|---|
| MPh | {MN15} | 1 | 1.44±0.01 | 1.43±0.05 | 1.41±0.05 | 0.01 | 177 |
| | [MN15] | 1 | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.03 | 176 |
| | MN15– | 1 | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.03 | 175 |
| | MN15 | 1 | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.03 | 175 |
| | MN15+ | 1 | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.03 | 176 |
| | MN15cc | 1 | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.03 | 176 |
| | MP2 | 1 | 1.54±0.00 | 1.40±0.05 | 1.41±0.05 | 0.03 | 171 |
| | MP4$^{SDQ}$ | 1 | 1.43±0.01 | 1.42±0.04 | 1.40±0.04 | 0.05 | 173 |
| | CCSD | 1 | 1.43±0.01 | 1.42±0.04 | 1.40±0.04 | 0.04 | 173 |
| | {MN15} | 2 | 1.44±0.01 | 1.43±0.05 | 1.41±0.05 | 0.00 | 177 |
| | [MN15] | 2 | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.00 | 177 |
| | MN15– | 2 | 1.43±0.00 | 1.42±0.04 | 1.40±0.04 | 0.00 | 176 |
| | MN15 | 2 | 1.43±0.00 | 1.42±0.04 | 1.39±0.04 | 0.00 | 176 |
| | MN15+ | 2 | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.00 | 176 |
| | MN15cc | 2 | 1.42±0.00 | 1.41±0.04 | 1.39±0.04 | 0.00 | 176 |
| B-MPh | {MN15} | 1 | 1.52±0.01 | 1.44±0.05 | 1.43±0.05 | 0.00 | 174 |
| | [MN15] | 1 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.02 | 173 |
| | MN15– | 1 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.04 | 172 |
| | MN15 | 1 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.04 | 172 |
| | MN15+ | 1 | 1.52±0.01 | 1.41±0.04 | 1.41±0.04 | 0.04 | 172 |
| | MN15cc | 1 | 1.52±0.01 | 1.41±0.04 | 1.41±0.04 | 0.04 | 172 |
| | MP2 | 1 | 1.54±0.00 | 1.40±0.05 | 1.41±0.05 | 0.03 | 171 |
| | MP4$^{SDQ}$ | 1 | 1.54±0.00 | 1.41±0.04 | 1.42±0.04 | 0.02 | 173 |
| | CCSD | 1 | 1.54±0.01 | 1.42±0.05 | 1.42±0.05 | 0.04 | 171 |
| | {MN15} | 2 | 1.52±0.01 | 1.43±0.05 | 1.43±0.05 | 0.00 | 174 |
| | [MN15] | 2 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.00 | 173 |
| | MN15– | 2 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.00 | 172 |
| | MN15 | 2 | 1.52±0.01 | 1.42±0.04 | 1.41±0.04 | 0.00 | 172 |
| | MN15+ | 2 | 1.52±0.01 | 1.41±0.04 | 1.41±0.04 | 0.00 | 172 |
| | MN15cc | 2 | 1.52±0.01 | 1.41±0.04 | 1.41±0.04 | 0.00 | 172 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N-MPh | {MN15} | 1 | 1.44±0.01 | 1.44±0.05 | 1.41±0.04 | 0.01 | 179 |
| | [MN15] | 1 | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.03 | 178 |
| | MN15− | 1 | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.03 | 175 |
| | MN15 | 1 | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.02 | 177 |
| | MN15+ | 1 | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.02 | 178 |
| | MN15cc | 1 | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.02 | 178 |
| | MP2 | 1 | 1.41±0.01 | 1.41±0.01 | 1.39±0.03 | 0.01 | 175 |
| | MP4$^{SDQ}$ | 1 | 1.41±0.01 | 1.42±0.02 | 1.39±0.03 | 0.01 | 176 |
| | CCSD | 1 | 1.42±0.01 | 1.42±0.07 | 1.41±0.05 | 0.07 | 169 |
| | {MN15} | 2 | 1.44±0.0 | 1.44±0.05 | 1.41±0.04 | 0.00 | 179 |
| | [MN15] | 2 | 1.41±0.0 | 1.42±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15− | 2 | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15 | 2 | 1.41±0.01 | 1.42±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15+ | 2 | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.00 | 179 |
| | MN15cc | 2 | 1.40±0.01 | 1.41±0.04 | 1.39±0.03 | 0.00 | 179 |

**Table S5.** Adsorption model structures (LoT: MN15 using the STO-3G {MN15}, SDDAll [MN15], 6-31G* (MN15−), or def2-QZVPP (MN15+), or *aug-cc*-pVTZ (MN15cc) basis sets) of methane on MPh, B-MPh, and N-MPh. Adsorption by one (n = 1) and two (n = 2) methane molecules is described by interaction distances and twisting angles: methane to central site (C25···X1) distance, proximal H to closest ring centroid ($H_p$···$X_i$) distance, dihedral angle formed by $X_i$···X1···C25–$H_p$ (ω), and proximal and distal C–H bond lengths.

| Adsorbent | LoT | n | C25···X1, Å | $H_p$···$X_i$, Å | ω, ° | C–$H_p$,[a] Å | C–$H_d$,[a] Å |
|---|---|---|---|---|---|---|---|
| MPh | {MN15} | 1 | 3.44 | 3.09±0.20 | 2±1 | 1.096±0.000 | 1.096 |
| | [MN15] | 1 | 3.29 | 2.92±0.03 | 0±1 | 1.091±0.000 | 1.090 |
| | MN15− | 1 | 3.28 | 2.90±0.04 | 1±1 | 1.094±0.000 | 1.093 |
| | MN15+ | 1 | 3.28 | 2.91±0.04 | 0±0 | 1.089±0.000 | 1.087 |
| | MN15cc | 1 | 3.28 | 2.91±0.04 | 0±0 | 1.089±0.000 | 1.087 |
| | {MN15} | 2 | 3.56±0.01 | 3.23±0.38 | 10±4 | 1.096±0.000 | 1.096±0.000 |
| | [MN15] | 2 | 3.29±0.00 | 2.95±0.02 | 1±0 | 1.091±0.000 | 1.090±0.000 |
| | MN15− | 2 | 3.27±0.00 | 2.93±0.03 | 1±1 | 1.094±0.000 | 1.093±0.000 |
| | MN15+ | 2 | 3.27±0.00 | 2.93±0.03 | 1±0 | 1.089±0.000 | 1.087±0.000 |
| | MN15cc | 2 | 3.27±0.00 | 2.93±0.03 | 1±0 | 1.089±0.000 | 1.087±0.000 |
| B-MPh | {MN15} | 1 | 3.45 | 3.11±0.28 | 2±1 | 1.096±0.000 | 1.096 |
| | [MN15] | 1 | 3.28 | 2.91±0.04 | 4±1 | 1.091±0.000 | 1.090 |
| | MN15− | 1 | 3.29 | 2.91±0.05 | 3±1 | 1.094±0.000 | 1.093 |
| | MN15+ | 1 | 3.30 | 2.93±0.05 | 5±1 | 1.088±0.000 | 1.087 |
| | MN15cc | 1 | 3.30 | 2.93±0.05 | 5±1 | 1.088±0.000 | 1.087 |
| | {MN15} | 2 | 3.44±0.01 | 3.10±0.23 | 6±2 | 1.096±0.000 | 1.096±0.000 |
| | [MN15] | 2 | 3.26±0.00 | 2.92±0.04 | 4±1 | 1.091±0.000 | 1.090±0.000 |
| | MN15− | 2 | 3.27±0.00 | 2.93±0.05 | 2±1 | 1.094±0.000 | 1.093±0.000 |
| | MN15+ | 2 | 3.29±0.00 | 2.95±0.04 | 4 ±1 | 1.088±0.000 | 1.087±0.000 |
| | MN15cc | 2 | 3.29±0.00 | 2.95±0.04 | 4 ±1 | 1.088±0.000 | 1.087±0.000 |
| N-MPh | {MN15} | 1 | 3.28 | 2.93±0.01 | 0±0 | 1.096±0.000 | 1.096 |
| | [MN15] | 1 | 3.17 | 2.82±0.01 | 7±11 | 1.091±0.000 | 1.089 |
| | MN15− | 1 | 3.17 | 2.80±0.01 | 1±1 | 1.095±0.000 | 1.093 |
| | MN15+ | 1 | 3.17 | 2.81±0.00 | 1±1 | 1.089±0.000 | 1.087 |
| | MN15cc | | | | | | |
| | {MN15} | 2 | 3.28±0.00 | 2.94±0.01 | 1±0 | 1.096±0.000 | 1.096±0.000 |
| | [MN15] | 2 | 3.17±0.00 | 2.83±0.01 | 1±1 | 1.091±0.000 | 1.089±0.000 |
| | MN15− | 2 | 3.16±0 | 2.82±0.01 | 1±1 | 1.095±0.000 | 1.093±0.000 |
| | MN15+ | 2 | 3.16±0.00 | 2.82±0.01 | 1±1 | 1.089±0.000 | 1.087±0.000 |
| | MN15cc | 2 | 3.16±0.00 | 2.82±0.01 | 1±1 | 1.089±0.000 | 1.087±0.000 |

[a]The C–H bond lengths in free methane are, at {MN15}: 1.095 Å, [MN15]: 1.089 Å, MN15−: 1.092 Å; MN15+: 1.086 Å; and MN15cc: 1.087 Å

**Table S6.** Desorption energies ($\Delta_{des}$, kJ mol$^{-1}$) for MPh×nCH$_4$ → MPh + nCH$_4$ (LoT: MN15 using the STO-3G {MN15}, SDDAll [MN15], 6-31G* (MN15–), def2-QZVPP (MN15+), or *aug-cc*-pVTZ (MN15cc) basis sets). mCBS-QB3 refers to the modified complete basis set extrapolation method employing the CBS-QB3 formalism, but utilizing the MN15/6-311++G** geometry (see Table S6.5 for details). The standard enthalpy, Gibbs free energy, and entropy of desorption are calculated at 298 K using a simple statistical mechanical model assuming ideal gas behavior. A modest statistical analysis (average and standard deviation) of the thermochemical quantities is shown, normalized per mole of CH$_4$.

| Adsorbent | n | $\Delta_{des}U^{QM}$ (kJ mol$^{-1}$) | | | | | | BSSE (kJ mol$^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | {MN15} | [MN15] | MN15– | MN15+ | MN15cc | mCBS-QB3 | {MN15} | [MN15] | MN15– | MN15+ | MN15cc |
| MPh | 1 | 3 | 16 | 13 | 14 | 15 | 10 | 2.5 | 2.8 | 3.7 | 0.3 | 1.5 |
| B-MPh | 1 | 2 | 13 | 14 | 13 | 15 | 9 | 1.9 | 2.2 | 4.4 | 0.2 | 1.7 |
| N-MPh | 1 | 3 | 17 | 16 | 16 | 18 | 12 | 2.3 | 2.6 | 3.9 | 0.3 | 1.8 |
| | | | | | | | | | | | | |
| MPh | 2 | 5 | 33 | 26 | 27 | 31 | 21 | 5.0 | 5.7 | 7.2 | 0.6 | 3.7 |
| B-MPh | 2 | 4 | 25 | 26 | 26 | 29 | 18 | 4.2 | 4.3 | 8.3 | 0.5 | 4.1 |
| N-MPh | 2 | 5 | 33 | 32 | 32 | 36 | 24 | 4.6 | 5.1 | 7.4 | 0.6 | 4.1 |
| | | | | | | | | | | | | |
| MPh | per CH$_4$ | 2.5±0.0 | 16.3±0.0 | 13.0±0.2 | 13.6±0.3 | 15.3±0.0 | 10.2±0.2 | | | | | |
| B-MPh | per CH$_4$ | 2.0±0.1 | 12.8±0.3 | 13.3±0.2 | 13.2±0.3 | 14.6±0.1 | 8.9±0.1 | | | | | |
| N-MPh | per CH$_4$ | 2.7±0.0 | 16.5±0.2 | 16.2±0.4 | 16.2±0.2 | 18.0±0.0 | 12.2±0.0 | | | | | |

| Adsorbent | n | $\Delta_{des}H°$ (kJ mol$^{-1}$) | | | | | | $\Delta_{des}G°$ (kJ mol$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | {MN15} | [MN15] | MN15– | MN15+ | MN15cc | mCBS-QB3 | {MN15} | [MN15] | MN15– | MN15+ | MN15cc | mCBS-QB3 |
| MPh | 1 | -3 | 11 | 8 | 9 | 11 | 9 | -28 | -23 | -28 | -26 | -24 | -19 |
| B-MPh | 1 | -3 | 8 | 9 | 9 | 10 | 7 | -31 | -27 | -26 | -25 | -23 | -19 |
| N-MPh | 1 | -3 | 12 | 9 | 11 | 13 | 9 | -40 | -26 | -23 | -25 | -22 | -12 |
| | | | | | | | | | | | | | |
| MPh | 2 | -3 | 23 | 16 | 16 | 21 | 18 | -62 | -46 | -54 | -51 | -48 | -34 |
| B-MPh | 2 | -6 | 15 | 17 | 17 | 20 | 14 | -56 | -53 | -51 | -50 | -47 | -35 |
| N-MPh | 2 | -7 | 23 | 21 | 22 | 26 | 22 | -80 | -51 | -53 | -50 | -46 | -35 |
| | | | | | | | | | | | | | |
| MPh | per CH$_4$ | -1.9±0.9 | 11.5±0.0 | 7.9±0.2 | 8.7±0.3 | 10.7±0.2 | 8.8±0.0 | -29.3±2.3 | -23.1±0.2 | -27.3±0.6 | -13.1±0.6 | -23.8±0.1 | -18.0±1.0 |
| B-MPh | per CH$_4$ | -3.2±0.2 | 7.8±0.2 | 8.4±0.2 | 8.4±0.3 | 10.1±0.2 | 7.2±0.0 | -29.8±2.2 | -26.8±0.4 | -26.0±0.4 | -12.6±0.3 | -23.4±0.2 | -18.2±1.5 |
| N-MPh | per CH$_4$ | -3.4±0.1 | 11.4±0.2 | 9.6±1.5 | 11.2±0.2 | 13.3±0.2 | 9.9±1.6 | -40.0±0.1 | -25.7±0.3 | -24.9±2.3 | -12.7±0.3 | -22.6±0.3 | -14.5±4.2 |

**Table S7.** Energy components of the modified CBS-QB3 method using fixed MN15/6-311++G** equilibrium structures for adsorbent, adsorbate, and adsorption models and corresponding vibrational analyses (invoking Gaussian keyword 'StartMP2' and using the results of the frequency calculation from the converged MN15 checkpoints).

| CBS-QB3 (StartMP2:MN15) | MN15/6-311G(2d,d,p) w/5d&7f | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E^{nuc.rep}$, a.u. | $E^{SCF}$, a.u. | $<S^2>$ before | after | $E^{ZPE}$, a.u. | $Q$, a.u. | $H$, a.u. | $G$, a.u. | $S$, cal/molK |
| $CH_4$ | 13.4425 | -40.5337 | 0.00 | 0.00 | -40.4891 | -40.4862 | -40.4853 | -40.5064 | 44.5 |
| B-MPh | 754.5442 | -526.3362 | 0.78 | 0.75 | -526.1510 | -526.1408 | -526.1399 | -526.1873 | 99.8 |
| MPh | 787.1806 | -539.6350 | 0.00 | 0.00 | -539.4457 | -539.4360 | -539.4351 | -539.4813 | 97.3 |
| N-MPh | 812.5538 | -556.2317 | 0.77 | 0.75 | -556.0449 | -556.0357 | -556.0348 | -556.0796 | 94.4 |
| B-MPh×$CH_4$ | 888.0026 | -566.8668 | 0.78 | 0.75 | -566.6356 | -566.6213 | -566.6204 | -566.6779 | 121.1 |
| MPh×$CH_4$ | 923.5009 | -580.1662 | 0.00 | 0.00 | -579.9307 | -579.9170 | -579.9160 | -579.9718 | 117.4 |
| N-MPh×$CH_4$ | 953.3618 | -596.7628 | 0.77 | 0.75 | -596.5296 | -596.5156 | -596.5146 | -596.5721 | 120.9 |
| B-MPh×2$CH_4$ | 1027.9738 | -607.3976 | 0.78 | 0.75 | -607.1207 | -607.1019 | -607.1010 | -607.1706 | 146.5 |
| MPh×2$CH_4$ | 1066.4851 | -620.6976 | 0.00 | 0.00 | -620.4162 | -620.3982 | -620.3972 | -620.4650 | 142.6 |
| N-MPh×2$CH_4$ | 1101.6539 | -637.2941 | 0.77 | 0.75 | -637.0149 | -636.9976 | -636.9966 | -637.0610 | 135.6 |

| CBS-QB3 (StartMP2:MN15) | CCSD(T)/6-31+G(d') w/6d&7f | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $E^{SCF}$, a.u. | $<S^2>$ before | after | $E^{MP2}$, a.u. | $E^{MP3}$, a.u. | $E^{MP4sdq}$, a.u. | $E^{CCSD}$, a.u. | $E^{CCSD(T)}$, a.u. |
| $CH_4$ | -40.1954 | 0.00 | 0.00 | -40.3359 | -40.3525 | -40.3561 | -40.3568 | -40.3597 |
| B-MPh | -522.7987 | 2.48 | 4.93 | -524.3961 | -524.4858 | -524.5127 | -524.5466 | -524.6339 |
| MPh | -535.9817 | 0.00 | 0.00 | -537.7811 | -537.8228 | -537.8343 | -537.8357 | -537.9302 |
| N-MPh | -552.5321 | 2.44 | 4.70 | -554.2292 | -554.3089 | -554.3377 | -554.3735 | -554.4669 |
| B-MPh×$CH_4$ | -562.9909 | 2.48 | 4.93 | -564.7377 | -564.8431 | -564.8736 | -564.9080 | -564.9990 |
| MPh×$CH_4$ | -576.1732 | 0.00 | 0.00 | -578.1241 | -578.1802 | -578.1953 | -578.1973 | -578.2960 |
| N-MPh×$CH_4$ | -592.7234 | 2.44 | 4.68 | -594.5722 | -594.6670 | -594.6994 | -594.7361 | -594.8339 |
| B-MPh×2$CH_4$ | -603.1836 | 2.48 | 4.93 | -605.0798 | -605.2009 | -605.2350 | -605.2698 | -605.3645 |
| MPh×2$CH_4$ | -616.3653 | 0.00 | 0.00 | -618.4667 | -618.5375 | -618.5563 | -618.5588 | -618.6616 |
| N-MPh×2$CH_4$ | -632.9153 | 2.44 | 4.67 | -634.9153 | -635.0253 | -635.0614 | -635.0988 | -635.2009 |

| CBS-QB3 (StartMP2:MN15) | MP4SDQ/CBSB4 w/6d&7f | | | | | | MP2/CBSB3 w/5d&7f | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E^{SCF}$, a.u. | $<S^2>$ before | after | $E^{MP2}$, a.u. | $E^{MP3}$, a.u. | $E^{MP4sdq}$, a.u. | $E^{SCF}$, a.u. | $<S^2>$ before | after | $E^{MP2}$, a.u. |
| $CH_4$ | -40.2010 | 0.00 | 0.00 | -40.3675 | -40.3870 | -40.3896 | -40.2122 | 0.00 | 0.00 | -40.4043 |
| B-MPh | -522.8146 | 2.47 | 4.91 | -524.4734 | -524.5691 | -524.5934 | -522.9430 | 2.47 | 4.89 | -524.8981 |
| MPh | -535.9981 | 0.00 | 0.00 | -537.8585 | -537.9058 | -537.9144 | -536.1318 | 0.00 | 0.00 | -538.3024 |
| N-MPh | -552.5487 | 2.44 | 4.68 | -554.3070 | -554.3924 | -554.4187 | -552.6910 | 2.43 | 4.63 | -554.7694 |
| B-MPh×$CH_4$ | -563.0123 | 2.47 | 4.92 | -564.8465 | -564.9604 | -564.9874 | -563.1520 | 2.47 | 4.90 | -565.3077 |
| MPh×$CH_4$ | -576.1952 | 0.00 | 0.00 | -578.2331 | -578.2974 | -578.3087 | -576.3402 | 0.00 | 0.00 | -578.7136 |
| N-MPh×$CH_4$ | -592.7455 | 2.44 | 4.66 | -594.6817 | -594.7848 | -594.8138 | -592.8989 | 2.43 | 4.62 | -595.1803 |
| B-MPh×2$CH_4$ | -603.2106 | 2.47 | 4.91 | -605.2197 | -605.3520 | -605.3816 | -603.3615 | 2.47 | 4.90 | -605.7178 |
| MPh×2$CH_4$ | -616.3928 | 0.00 | 0.00 | -618.6072 | -618.6888 | -618.7028 | -616.5493 | 0.00 | 0.00 | -619.1250 |
| N-MPh×2$CH_4$ | -632.9430 | 2.43 | 4.65 | -635.0563 | -635.1771 | -635.2090 | -633.1075 | 2.43 | 4.61 | -635.5915 |

| CBS-QB3 (StartMP2:MN15) | ElSum | E2(CBS) | CBS-Int | OTii | E(ZPE) | E(thermal) | CBS-MN15 technical E(SCF) | ΔE(MP2) | ΔE(CBS) | ΔE(MP34) | ΔE(CCSD) | ΔE(Int) | ΔE(empirical) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CH₄ | 5.0 | -0.2114 | 0.0073 | 2.0796 | 0.0442 | 0.0471 | -40.2122 | -0.1920 | -0.0194 | -0.0222 | -0.0036 | 0.0073 | -0.0120 |
| B-MPh | 93.0 | -2.1436 | 0.0617 | 15.5321 | 0.1864 | 0.1968 | -522.9431 | -1.9550 | -0.1886 | -0.1200 | -0.1212 | 0.0617 | -0.1063 |
| MPh | 47.0 | -2.3729 | 0.0698 | 16.2389 | 0.1906 | 0.2005 | -536.1318 | -2.1706 | -0.2023 | -0.0559 | -0.0960 | 0.0698 | -0.0940 |
| N-MPh | 95.0 | -2.2800 | 0.0642 | 16.2173 | 0.1878 | 0.1972 | -552.6910 | -2.0784 | -0.2016 | -0.1117 | -0.1293 | 0.0642 | -0.1099 |
| B-MPh×CH₄ | 103.0 | -2.3639 | 0.0691 | 17.5837 | 0.2319 | 0.2468 | -563.1520 | -2.1558 | -0.2081 | -0.1409 | -0.1255 | 0.0691 | -0.1182 |
| MPh×CH₄ | 52.0 | -2.5952 | 0.0772 | 18.2867 | 0.2364 | 0.2505 | -576.3402 | -2.3734 | -0.2218 | -0.0756 | -0.1007 | 0.0772 | -0.1059 |
| N-MPh×CH₄ | 105.0 | -2.5026 | 0.0717 | 18.2664 | 0.2337 | 0.2482 | -592.8989 | -2.2814 | -0.2211 | -0.1321 | -0.1345 | 0.0717 | -0.1218 |
| B-MPh×2CH₄ | 113.0 | -2.5835 | 0.0764 | 19.6337 | 0.2774 | 0.2967 | -603.3615 | -2.3564 | -0.2271 | -0.1619 | -0.1296 | 0.0764 | -0.1301 |
| MPh×2CH₄ | 57.0 | -2.8164 | 0.0845 | 20.3359 | 0.2819 | 0.3006 | -616.5493 | -2.5756 | -0.2407 | -0.0955 | -0.1054 | 0.0845 | -0.1177 |
| N-MPh×2CH₄ | 115.0 | -2.7241 | 0.0789 | 20.3144 | 0.2794 | 0.2973 | -633.1075 | -2.4840 | -0.2400 | -0.1527 | -0.1395 | 0.0789 | -0.1336 |

| CBS-QB3 (StartMP2:MN15) | CBS-MN15 (NoOpt) final at 298.15 K 1 atm | | | |
|---|---|---|---|---|
| | (0 Kelvin) | U, a.u. | H, a.u. | G, a.u. |
| CH₄ | -40.4099 | -40.4071 | -40.4061 | -40.4273 |
| B-MPh | -525.1861 | -525.1757 | -525.1748 | -525.2225 |
| MPh | -538.4902 | -538.4804 | -538.4794 | -538.5259 |
| N-MPh | -555.0698 | -555.0604 | -555.0595 | -555.1046 |
| B-MPh×CH₄ | -565.5994 | -565.5846 | -565.5837 | -565.6425 |
| MPh×CH₄ | -578.9040 | -578.8898 | -578.8889 | -578.9459 |
| N-MPh×CH₄ | -595.4844 | -595.4699 | -595.4689 | -595.5274 |
| B-MPh×2CH₄ | -606.0128 | -605.9935 | -605.9925 | -606.0637 |
| MPh×2CH₄ | -619.3180 | -619.2993 | -619.2984 | -619.3676 |
| N-MPh×2CH₄ | -635.8990 | -635.8811 | -635.8802 | -635.9458 |

**Table S8.** Energy stabilization ($\Delta\Delta E^{QM}$) and desorption ($\rightarrow$MPh+CH$_4$) energy differences (in kJ mol$^{-1}$) due to optimizing the MN16/6-311++G** equilibrium structures of the adsorbent, adsorbate, and the adsorption model using a conceptually converging series of correlated MO theories (LoT: MP2, MP3, MP4, CCSD, or CCSD(T) using the 6-311++G** basis set).

| $\Delta\Delta E^{QM}$ | MP2 | MP3 | MP4[a] | CCSD | CCSD(T)[b] |
|---|---|---|---|---|---|
| MPh | -10 | -5 | -10 | -6 | -9 |
| B-MPh | -10 | -8 | -9 | -7 | -7 |
| N-MPh | -13 | -9 | -15 | -11 | -10 |
| | | | | | |
| CH$_4$ | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | | | | | |
| MPh×CH$_4$ | -9 | -5 | -8 | -5 | -8 |
| B-MPh×CH$_4$ | -9 | -8 | -9 | -7 | -6 |
| N-MPh×CH$_4$ | -10 | -10 | -9 | -8 | -12 |
| | | | | | |
| $\rightarrow$MPh+CH$_4$ | -1 | 0 | -2 | -1 | -1 |
| $\rightarrow$B-MPh+CH$_4$ | -1 | 0 | 0 | 0 | -1 |
| $\rightarrow$N-MPh+CH$_4$ | -3 | +2 | -6 | -3 | +2 |

[a]MP4 results are single-point energy calculations using the MP4$^{SDQ}$ geometry (i.e., MP4|MP4$^{SDQ}$).
[b]CCSD(T) results are single-point energy calculations using the CCSD geometry (i.e., CCSD(T)|CCSD)

**Table S9.** Atomic charge (electron) distribution analysis upon single (n = 1) and double (n = 2) methane adsorption on MPh, B-MPh, and N-MPh determined by three conceptually different population analysis methods: Hirshfeld (HPA), Weinhold (NPA), and Merz-Kollman (ESP) at the MN15/def2-QZVPP level of theory. See **Figure 2** for a graphical plot and **Figure S1** for the numbering of atom positions.

| X | n | X1 | α | | C4 | C5 | C6 | β | | | | | γ | | =CH$_2$ | Σ H |
| | | | C2 | C3 | | | | C7 | C8 | C9 | C10 | C11 | C12 | C13 | C14 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hirshfeld Population Analysis (HPA) | | | | | | | | | | | | | | | | |
| C | 1 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | -0.03 | -0.03 | -0.04 | -0.04 | -0.04 | -0.04 | -0.04 | -0.04 | -0.08 | 0.39 |
| B | 1 | 0.04 | -0.08 | -0.07 | -0.04 | 0.01 | 0.00 | -0.02 | 0.00 | -0.03 | -0.02 | 0.00 | -0.05 | -0.02 | -0.05 | 0.37 |
| N | 1 | 0.04 | 0.07 | 0.06 | 0.04 | -0.02 | -0.07 | -0.05 | -0.08 | -0.05 | -0.07 | -0.05 | -0.02 | -0.04 | -0.11 | 0.39 |
| C | 2 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | -0.03 | -0.03 | -0.03 | -0.03 | -0.03 | -0.04 | -0.04 | -0.04 | -0.08 | 0.40 |
| B | 2 | 0.05 | -0.08 | -0.07 | -0.04 | 0.01 | 0.00 | -0.02 | 0.00 | -0.03 | -0.02 | 0.00 | -0.05 | -0.02 | -0.05 | 0.38 |
| N | 2 | 0.05 | 0.07 | 0.07 | 0.04 | -0.02 | -0.07 | -0.05 | -0.08 | -0.05 | -0.07 | -0.05 | -0.02 | -0.04 | -0.11 | 0.40 |
| Weinhold Natural Population Analysis (NPA) | | | | | | | | | | | | | | | | |
| C | 1 | -0.03 | -0.04 | -0.06 | -0.06 | -0.08 | -0.18 | -0.18 | -0.18 | -0.19 | -0.18 | -0.18 | -0.21 | -0.21 | -0.34 | 2.12 |
| B | 1 | 0.61 | -0.39 | -0.37 | -0.26 | -0.08 | -0.09 | -0.14 | -0.11 | -0.20 | -0.17 | -0.11 | -0.25 | -0.19 | -0.29 | 2.05 |
| N | 1 | -0.33 | 0.23 | 0.20 | 0.13 | -0.13 | -0.29 | -0.25 | -0.30 | -0.23 | -0.26 | -0.20 | -0.15 | -0.20 | -0.41 | 2.17 |
| C | 2 | -0.02 | -0.04 | -0.06 | -0.06 | -0.08 | -0.18 | -0.18 | -0.18 | -0.19 | -0.18 | -0.18 | -0.21 | -0.21 | -0.34 | 2.12 |
| B | 2 | 0.67 | -0.41 | -0.39 | -0.28 | -0.08 | -0.10 | -0.15 | -0.12 | -0.21 | -0.18 | -0.11 | -0.25 | -0.18 | -0.29 | 2.06 |
| N | 2 | -0.34 | 0.24 | 0.21 | 0.14 | -0.13 | -0.30 | -0.26 | -0.30 | -0.23 | -0.26 | -0.20 | -0.15 | -0.20 | -0.41 | 2.18 |
| Merz-Kollman Electrostatic Potential Fit (ESP) | | | | | | | | | | | | | | | | |
| C | 1 | -0.02 | 0.04 | 0.28 | 0.17 | 0.20 | -0.19 | -0.29 | -0.35 | -0.26 | -0.23 | -0.19 | -0.08 | -0.03 | -0.51 | 1.48 |
| B | 1 | 0.24 | -0.25 | -0.07 | 0.03 | 0.24 | 0.02 | -0.13 | -0.09 | -0.21 | -0.13 | -0.19 | -0.23 | -0.12 | -0.43 | 1.32 |
| N | 1 | 0.25 | 0.06 | 0.16 | 0.15 | 0.15 | -0.29 | -0.31 | -0.32 | -0.30 | -0.33 | -0.15 | -0.01 | -0.07 | -0.60 | 1.62 |
| C | 2 | 0.72 | -0.27 | 0.01 | -0.11 | 0.25 | -0.10 | -0.24 | -0.29 | -0.20 | -0.19 | -0.25 | -0.16 | -0.10 | -0.50 | 1.51 |
| B | 2 | 0.96 | -0.49 | -0.27 | -0.13 | 0.23 | 0.05 | -0.12 | -0.11 | -0.22 | -0.18 | -0.18 | -0.28 | -0.14 | -0.41 | 1.39 |
| N | 2 | 1.48 | -0.46 | -0.28 | -0.32 | 0.25 | -0.18 | -0.25 | -0.24 | -0.21 | -0.26 | -0.23 | -0.09 | -0.16 | -0.59 | 1.66 |

**Table S10.** Atomic charge (electron) distribution analysis upon single (n = 1) and double (n = 2) methane adsorption on MPh, B-MPh, and N-MPh determined by three conceptually different population analysis methods: Hirshfeld (HPA), Weinhold (NPA), and Merz-Kollman (ESP) at the MN15/def2-QZVPP level of theory. See **Figure 2** for a graphical plot and **Figure S1** for the numbering of atom positions (numbering of the second adsorbate is logical).

| X | n | C25 | proximal H26 | H27 | H28 | distal H29 | Σ CH$_4$ | C30 | H31 | proximal H32 | H33 | distal H34 | Σ CH$_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hirshfeld Population Analysis (HPA) | | | | | | | | | | | | | |
| C | 1 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.04 | | | | | | |
| B | 1 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.03 | | | | | | |
| N | 1 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.04 | | | | | | |
| C | 2 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.03 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.03 |
| B | 2 | -0.13 | 0.02 | 0.03 | 0.02 | 0.03 | -0.03 | -0.13 | 0.02 | 0.03 | 0.02 | 0.03 | -0.03 |
| N | 2 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.04 | -0.13 | 0.02 | 0.02 | 0.02 | 0.03 | -0.04 |
| Weinhold Natural Population Analysis (NPA) | | | | | | | | | | | | | |
| C | 1 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | | | | | | |
| B | 1 | -0.83 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | | | | | | |
| N | 1 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | | | | | | |
| C | 2 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 |
| B | 2 | -0.83 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | -0.83 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 |
| N | 2 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 | -0.84 | 0.21 | 0.21 | 0.21 | 0.21 | 0.00 |
| Merz-Kollman Electrostatic Potential Fit (ESP) | | | | | | | | | | | | | |
| C | 1 | -0.48 | 0.12 | 0.12 | 0.12 | 0.11 | -0.01 | | | | | | |
| B | 1 | -0.50 | 0.12 | 0.13 | 0.13 | 0.11 | 0.00 | | | | | | |
| N | 1 | -0.50 | 0.13 | 0.12 | 0.12 | 0.12 | -0.01 | | | | | | |
| C | 2 | -0.45 | 0.10 | 0.09 | 0.10 | 0.11 | -0.05 | -0.44 | 0.10 | 0.09 | 0.09 | 0.11 | -0.05 |
| B | 2 | -0.46 | 0.09 | 0.10 | 0.10 | 0.12 | -0.05 | -0.46 | 0.09 | 0.10 | 0.10 | 0.12 | -0.05 |
| N | 2 | -0.45 | 0.09 | 0.09 | 0.09 | 0.12 | -0.06 | -0.45 | 0.09 | 0.09 | 0.09 | 0.12 | -0.06 |

**Table S11.** Atomic spin densities of the adsorbent molecule for single (n = 1) and double (n = 2) methane adsorption on B-MPh and N-MPh from Hirshfeld population analysis (HPA) and Weinhold natural population analysis (NPA) at the MN15/def2-QZVPP level of theory. See **Figure S1** for the numbering of atom positions.

| X | n | X1 | α | | C4 | C5 | C6 | β | | | | | γ | | =CH$_2$ | Σ H |
|---|---|----|-----|-----|----|----|----|----|----|----|-----|-----|-----|-----|-----|-----|
| | | | C2 | C3 | | | | C7 | C8 | C9 | C10 | C11 | C12 | C13 | C14 | |
| Hirshfeld Population Analysis (HPA) | | | | | | | | | | | | | | | | |
| B | 1 | 0.10 | -0.01 | 0.05 | 0.18 | -0.02 | 0.08 | 0.03 | 0.06 | -0.02 | -0.03 | 0.21 | 0.01 | 0.14 | 0.17 | 0.05 |
| N | 1 | 0.03 | 0.00 | 0.02 | 0.13 | -0.01 | 0.11 | 0.07 | 0.09 | 0.02 | 0.00 | 0.15 | -0.01 | 0.09 | 0.22 | 0.07 |
| B | 2 | 0.11 | -0.01 | 0.05 | 0.18 | -0.02 | 0.07 | 0.03 | 0.05 | -0.03 | -0.03 | 0.21 | 0.02 | 0.15 | 0.16 | 0.04 |
| N | 2 | 0.03 | 0.00 | 0.02 | 0.13 | -0.01 | 0.11 | 0.07 | 0.09 | 0.02 | 0.00 | 0.15 | -0.01 | 0.09 | 0.23 | 0.07 |
| Weinhold Natural Population Analysis (NPA) | | | | | | | | | | | | | | | | |
| B | 1 | 0.11 | -0.04 | 0.04 | 0.26 | -0.08 | 0.11 | 0.04 | 0.06 | -0.08 | -0.10 | 0.30 | -0.01 | 0.19 | 0.23 | -0.03 |
| N | 1 | 0.03 | -0.03 | 0.00 | 0.19 | -0.08 | 0.17 | 0.10 | 0.12 | -0.01 | -0.06 | 0.22 | -0.04 | 0.12 | 0.32 | -0.04 |
| B | 2 | 0.11 | -0.03 | 0.06 | 0.26 | -0.08 | 0.10 | 0.03 | 0.04 | -0.09 | -0.10 | 0.30 | 0.01 | 0.21 | 0.22 | -0.03 |
| N | 2 | 0.03 | -0.03 | 0.00 | 0.18 | -0.08 | 0.17 | 0.10 | 0.12 | -0.01 | -0.06 | 0.22 | -0.04 | 0.11 | 0.32 | -0.04 |

**Table S12.** Atomic spin densities of the adsorbate molecule(s) for single (n = 1) and double (n = 2) methane adsorption on B-MPh and N-MPh from Hirshfeld population analysis (HPA) and Weinhold natural population analysis (NPA) at the MN15/def2-QZVPP level of theory. See **Figure S1** for the numbering of atom positions (numbering of the second adsorbate is logical).

| X | n | C25 | | proximal | | distal | Σ CH$_4$ | C30 | | proximal | | distal | Σ CH$_4$ |
|---|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | | H26 | H27 | H28 | H29 | | | H31 | H32 | H33 | H34 | |
| Hirshfeld Population Analysis (HPA) | | | | | | | | | | | | | |
| B | 1 | 0.003 | 0.001 | 0.001 | 0.002 | 0.001 | 0.007 | | | | | | |
| N | 1 | 0.001 | 0.001 | 0.001 | 0.001 | 0.000 | 0.003 | | | | | | |
| B | 2 | 0.004 | 0.001 | 0.001 | 0.002 | 0.001 | 0.008 | 0.004 | 0.001 | 0.001 | 0.002 | 0.001 | 0.008 |
| N | 2 | 0.001 | 0.001 | 0.001 | 0.001 | 0.000 | 0.003 | 0.001 | 0.001 | 0.001 | 0.001 | 0.000 | 0.003 |
| Weinhold Natural Population Analysis (NPA) | | | | | | | | | | | | | |
| B | 1 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | | | | | | |
| N | 1 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | | | | | |
| B | 2 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 |
| N | 2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

**Table S13.** Thermochemical quantities (in kJ mol$^{-1}$) for comparison to experimental measurements of physisorptive binding of methane on porous carbon surfaces at 298 K. LoT: MN15/6-311++G**. MPh×CH$_4$ corresponds to 5.6 mmol g$^{-1}$ of absolute uptake and MPh×2CH$_4$ corresponds to 11.2 mmol g$^{-1}$, where uptake is defined as the true or "absolute" quantity. At room temperature (298 K), this corresponds to the following equilibrium pressures for adsorption on ZTC: 9.5 and 26.8 bar (or 9.3 and 26.4 atm), respectively. The enthalpy of desorption ($\Delta$H) at these conditions is measured to be 13.5 and 13.1 kJ mol$^{-1}$, respectively (Stadie et al., 2015 – Reference 48).

| System | P atm | $\Delta_{des}E^{QM*}$ kJ mol$^{-1}$ | $\Delta_{des}E_{ZPE}$ kJ mol$^{-1}$ | $\Delta_{des}U^{SM}$ kJ mol$^{-1}$ | $\Delta_{des}U^a$ kJ mol$^{-1}$ | $\Delta_{des}U^b$ kJ mol$^{-1}$ | $\Delta_{des}H^a$ kJ mol$^{-1}$ | $\Delta_{des}H^b$ kJ mol$^{-1}$ | $\Delta_{des}H^c$ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| MPh×CH$_4$ | 1 | 14.8 | -4.0 | -7.4 | 7.4 | 10.8 | 9.8 | 13.2 | 17.2 |
| B-MPh×CH$_4$ | 1 | 13.9 | -3.5 | -7.2 | 6.6 | 10.4 | 9.1 | 12.9 | 16.4 |
| N-MPh×CH$_4$ | 1 | 17.4 | -4.6 | -7.6 | 9.8 | 12.9 | 12.3 | 15.3 | 19.9 |
| MPh×CH$_4$ | 9.3 | 14.8 | -4.0 | -7.4 | 7.4 | 10.8 | 9.8 | 13.2 | 17.2 |
| B-MPh×CH$_4$ | 9.3 | 13.9 | -3.5 | -7.2 | 6.6 | 10.4 | 9.1 | 12.9 | 16.4 |
| N-MPh×CH$_4$ | 9.3 | 17.4 | -4.6 | -7.6 | 9.8 | 12.9 | 12.3 | 15.3 | 19.9 |
| MPh×2CH$_4$ | 26.4 | 14.1 | -4.1 | -7.6 | 6.6 | 10.1 | 9.1 | 12.5 | 16.6 |
| B-MPh×2CH$_4$ | 26.4 | 13.4 | -3.5 | -7.3 | 6.1 | 9.9 | 8.6 | 12.4 | 15.9 |
| N-MPh×2CH$_4$ | 26.4 | 17.0 | -4.4 | -7.6 | 9.4 | 12.6 | 11.9 | 15.1 | 19.5 |

[a] defined as $\Delta U^a = \Delta E^{QM*} + \Delta U^{SM}$ and $\Delta H^a = \Delta E^{QM*} + \Delta U^{SM} + RT$ referred to as $\Delta U°$ and $\Delta H°$ at P = 1 atm; [b] defined as $\Delta U^b = \Delta E^{QM*} + \Delta E_{ZPE}$ and $\Delta H^b = \Delta E^{QM*} + \Delta E_{ZPE} + \Delta PV$; [c] defined as $\Delta H^c = \Delta E^{QM*} + \Delta PV$

**Table S14.** Thermochemical quantities (in kJ mol$^{-1}$) for comparison to experimental measurements of physisorptive binding of methane on porous carbon surfaces at 298 K. LoT: MN15/def2-QZVPP. MPh×CH$_4$ corresponds to 5.6 mmol g$^{-1}$ of absolute uptake and MPh×2CH$_4$ corresponds to 11.2 mmol g$^{-1}$, where uptake is defined as the true or "absolute" quantity. At room temperature (298 K), this corresponds to the following equilibrium pressures for adsorption on ZTC: 9.5 and 26.8 bar (or 9.3 and 26.4 atm), respectively. The enthalpy of desorption ($\Delta_{des}H$) at these conditions is measured to be 13.5 and 13.1 kJ mol$^{-1}$, respectively (Stadie et al., 2015 – Reference 48).

| System | P atm | $\Delta_{des}E^{QM*}$ kJ mol$^{-1}$ | $\Delta_{des}E_{ZPE}$ kJ mol$^{-1}$ | $\Delta_{des}U^{SM}$ kJ mol$^{-1}$ | $\Delta_{des}U^a$ kJ mol$^{-1}$ | $\Delta_{des}U^b$ kJ mol$^{-1}$ | $\Delta_{des}H^a$ kJ mol$^{-1}$ | $\Delta_{des}H^b$ kJ mol$^{-1}$ | $\Delta_{des}H^c$ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| MPh×CH$_4$ | 1 | 13.6 | -3.8 | -7.4 | 6.1 | 9.8 | 8.6 | 12.2 | 16.0 |
| B-MPh×CH$_4$ | 1 | 13.1 | -3.4 | -7.3 | 5.8 | 9.7 | 8.3 | 12.2 | 15.6 |
| N-MPh×CH$_4$ | 1 | 16.1 | -4.2 | -7.5 | 8.6 | 11.9 | 11.0 | 14.4 | 18.6 |
| MPh×CH$_4$ | 9.3 | 13.6 | -3.8 | -7.4 | 6.1 | 9.8 | 8.6 | 12.2 | 16.0 |
| B-MPh×CH$_4$ | 9.3 | 13.1 | -3.4 | -7.3 | 5.8 | 9.7 | 8.3 | 12.2 | 15.6 |
| N-MPh×CH$_4$ | 9.3 | 16.1 | -4.2 | -7.5 | 8.6 | 11.9 | 11.0 | 14.4 | 18.6 |
| MPh×2CH$_4$ | 26.4 | 13.1 | -3.6 | -7.4 | 5.7 | 9.5 | 8.2 | 12.0 | 15.6 |
| B-MPh×2CH$_4$ | 26.4 | 12.8 | -3.3 | -7.3 | 5.5 | 9.5 | 8.0 | 12.0 | 15.2 |
| N-MPh×2CH$_4$ | 26.4 | 15.8 | -4.1 | -7.5 | 8.3 | 11.7 | 10.8 | 14.2 | 18.3 |

[a] defined as $\Delta U^a = \Delta E^{QM*} + \Delta U^{SM}$ and $\Delta H^a = \Delta E^{QM*} + \Delta U^{SM} + RT$ referred to as $\Delta U°$ and $\Delta H°$ at P = 1 atm; [b] defined as $\Delta U^b = \Delta E^{QM*} + \Delta E_{ZPE}$ and $\Delta H^b = \Delta E^{QM*} + \Delta E_{ZPE} + \Delta PV$; [c] defined as $\Delta H^c = \Delta E^{QM*} + \Delta PV$

**Table S15.** Consequences of the gradual relaxation of the $XC_{47}H_{20} \times CH_4$ (i.e., blade×$CH_4$ or X-blade×$CH_4$, X = B or N), adsorption model structures on $CH_4$ binding energies in kJ mol$^{-1}$, as a function of site of interaction (C, B, or N). A number of stationary structures (N) below 28 indicates a 'slip' of $CH_4$ into an adjacent adsorption site than originally targeted. Basis sets used for MN15–, MN15, and MN15 levels are 6-31G*, 6-311++G**, def2-QZVPP, respectively with the MN15 functional.

| | N | average | std. dev. | minimum | maximum |
|---|---|---|---|---|---|
| *Relaxation of peripheral H, CH$_4$: MN15– level* | | | | | |
| blade×CH$_4$ | 28 | 12.8 | 1.4 | 11 | 16 |
| B-blade×CH$_4$ | 28 | 12.7 | 1.5 | 11 | 16 |
| N-blade×CH$_4$ | 28 | 15.1 | 1.2 | 13 | 17 |
| *Relaxation of peripheral H, CH$_4$, site of adsorption: MN15– level* | | | | | |
| blade×CH$_4$ | 28 | 12.8 | 1.4 | 11 | 16 |
| B-blade×CH$_4$ | 28 | 12.8 | 1.6 | 10 | 16 |
| N-blade×CH$_4$ | 28 | 15.2 | 1.1 | 13 | 17 |
| *Relaxation of peripheral H, CH$_4$, site of adsorption, $\alpha$-carbons: MN15– level* | | | | | |
| blade×CH$_4$ | 30 | 13.2 | 1.7 | 11 | 17 |
| B-blade×CH$_4$ | 26 | 12.9 | 1.6 | 11 | 16 |
| N-blade×CH$_4$ | 28 | 15.2 | 0.9 | 13 | 17 |
| *Relaxation of peripheral H, CH$_4$, site of adsorption, $\alpha$-carbons: MN15–/MN15 level* | | | | | |
| blade×CH$_4$ | 30 | 17.7 | 1.9 | 14 | 21 |
| B-blade×CH$_4$ | 26 | 15.6 | 2.0 | 13 | 20 |
| N-blade×CH$_4$ | 28 | 18.9 | 1.3 | 16 | 21 |
| *Relaxation of peripheral H, CH$_4$, site of adsorption, $\alpha$-carbons: MN15 level* | | | | | |
| blade×CH$_4$ | 30 | 17.8 | 1.9 | 14 | 21 |
| B-blade×CH$_4$ | 26 | 15.9 | 2.3 | 13 | 20 |
| N-blade×CH$_4$ | 28 | 19.0 | 1.3 | 16 | 21 |
| *Relaxation of peripheral H, CH$_4$, site of adsorption, $\alpha$-carbons: MN15/MN15+ level* | | | | | |
| blade×CH$_4$ | 30 | 13.8 | 1.7 | 11 | 17 |
| B-blade×CH$_4$ | 26 | 12.9 | 1.7 | 10 | 15 |
| N-blade×CH$_4$ | 28 | 15.3 | 1.1 | 14 | 17 |