Edge Chemistry Effects on the Structural, Electronic, and Electric Response Properties of Boron Nitride Quantum Dots – Supporting Information

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Basis set convergence tests

Basis set convergence tests of the relative stability and electronic gap calculations have been performed for the hydrogenated 6x17 *h*-BNQD. The results of these calculations, which are summarized in Tab. S1, indicate that the relative structural stability energies and calculated electronic gaps are converged to within 3% and 2%, respectively, with respect to the choice of basis set.

Basis set	3-21G	6-31G**	6-311G**
δG (meV/atom)	59	63	61
Electronic gap (eV)	5.78	5.96	5.92

Table S1. Relative stability and electronic gap basis set convergence test. Comparison of δG values, calculated using Equation (1) of the main text, and ground state Kohn-Sham electronic HOMO-LUMO gaps of the hydrogenated 6x17 *h*-BNQD as calculated using the B3LYP exchange-correlation density functional approximation and the 3-21G, 6-31G** and 6-311G** Gaussian basis sets, are presented.

Furthermore, since the calculation of electric field response properties may be sensitive to the choice of atomic centered basis set and especially for the inclusion of diffuse functions we have repeated the calculations of the electric field response of the 6x17 *h*-BNQD using the 6-31++G** basis set. As can be seen in Fig. S1 the 6-31G** results are well converged also with respect to this property and therefore we have used them throughout the manuscript.

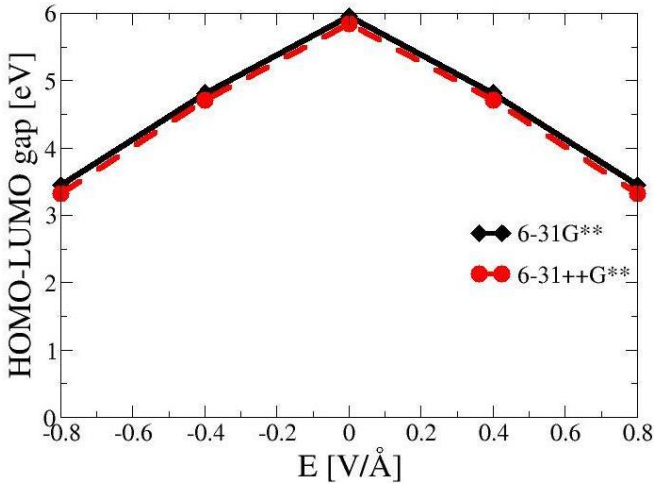

Fig. S1: Comparison of the HOMO-LUMO Kohn-Sham gap response of the 6x17 *h*-BNQD toward the application of an external electric field calculated using the double-ζ polarized 6-31G** basis set and its 6-31++G** diffuse counterpart.

Comparison of δG values calculated using several functional approximations

To verify consistency of our results we compare, in the left panel of Fig. S2, the B3LYP/6-31G** calculated δG values for the three hydrogenated *h*-BNQDs considered in the main text with similar calculations performed at the LDA and HSE[1-4] levels of theory. We find that, for all functional approximations used, the predicted stability of the *h*-BNQDs increases with their dimensions with LDA calculated stabilities being somewhat larger than the HSE and B3LYP values. The latter two functional approximations produce the same values for any practical matter. Furthermore, when considering larger *h*-BNQDs (right panel of Fig. S2) the same general trend of increased stability with system size is found.

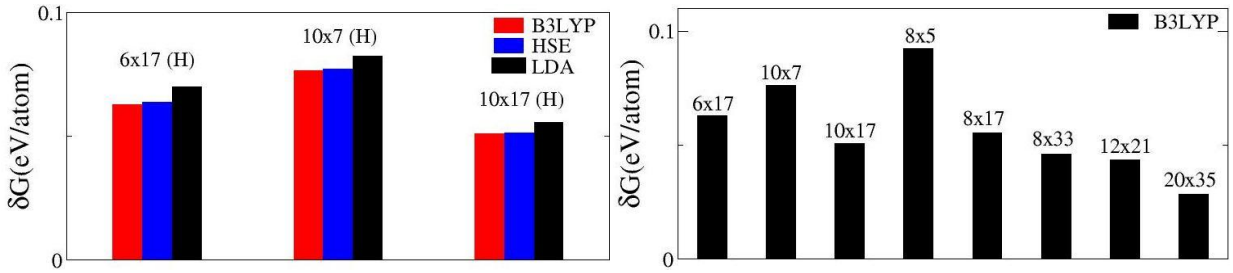

Fig. S2: Left – comparison of δG values obtained using the LDA, HSE, and B3LYP exchange-correlation density functional approximations for the three *h*-BNQDs considered in the main text. Right - δG values calculated at the B3LYP/6-31G** level of theory for a set of *h*-BNQDs with dimensions larger than those considered in the main text.

Comparison of calculated HOMO-LUMO gaps with previous studies

To verify consistency of our results we compare, in Fig. S3, our PBE/6-31G** and B3LYP/6-31G** calculated HOMO-LUMO gaps with the results obtained for the set of hydrogenated *h*-BNQDs considered by Yamijala et al.[5] As can be seen, our PBE results for these systems are in excellent agreement with those of Yamijala et al. thus providing good evidence for the consistency of our calculations. As may be expected, the hybrid B3LYP functional predicts larger gaps for all systems considered. Furthermore, we find weak dependence of the electronic gap value on the size of the system with the general expected trend of slight reduction in the gap with system size.

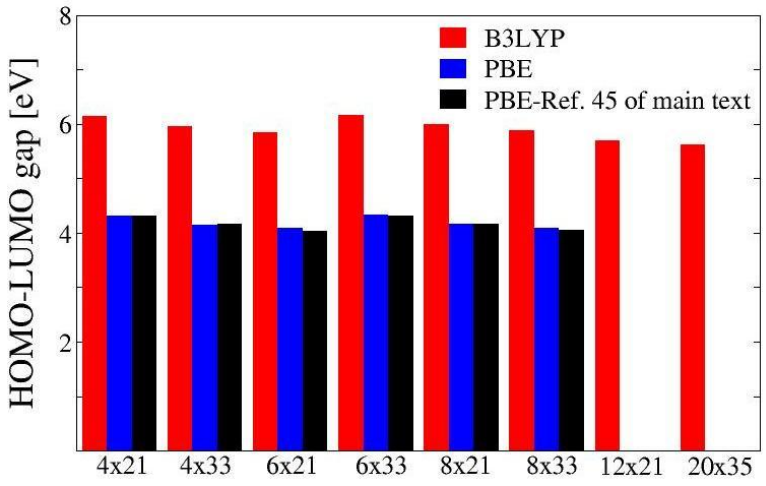

Fig. S3: Comparison of HOMO-LUMO gaps of various *h*-BNQDs calculated at the PBE/6-31G** and B3LYP/6-31G** levels of theory and results of Yamijala et al.[5]

References

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(2) Heyd, J.; Scuseria, G. E. Assessment and validation of a screened Coulomb hybrid density functional. J. Chem. Phys. 2004, 120, 7274-7280.
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(4) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: ``Hybrid functionals based on a screened Coulomb potential'' [J. Chem. Phys. 118, 8207 (2003)]. J. Chem. Phys. 2006, 124, 219906.
(5) Yamijala, S. S. R. K. C.; Bandyopadhyay, A.; Pati, S. K. Structural Stability, Electronic, Magnetic, and Optical Properties of Rectangular Graphene and Boron Nitride Quantum Dots: Effects of Size, Substitution, and Electric Field. J. Phys. Chem. C 2013, 117, 23295-23304.