Carlos-Andres Palma<sup>1</sup>, Manohar Awasthi<sup>2</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A. Niehaus<sup>2</sup> and Johannes V. Barth<sup>11</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany <sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

# Supporting Information for

# A Sub-nm Width Armchair Graphene Nanoribbon Energy Gap Atlas

Carlos-Andres Palma<sup>1‡</sup>, Manohar Awasthi<sup>2‡</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A.

Niehaus<sup>2</sup> and Johannes V. Barth<sup>1</sup>

<sup>1</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany

<sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany

<sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

‡Equally contributing authors.

# 1. Computational methods

Density-functional based tight-binding<sup>1</sup> (DFTB) calculations were performed with the DFTB+<sup>2</sup> package. DFTB is an approximate valence-only DFT method that employs localized atomic orbitals as basis functions. Details of the method can be found in a recent review<sup>1</sup>. Several benchmark studies are also available, which analyze the accuracy of DFTB with respect to energetical, structural and vibrational properties<sup>3-5</sup>.

In the present work, carbon was represented by one 2s and three 2p functions and hydrogen by a single 1s function as provided by the mio-0-1 Slater-Koster parameter set<sup>6</sup>. Each of these basis functions is a fixed linear combination of several Slater-type orbitals<sup>6, 7</sup>. All calculations were performed in the gas phase without using periodic boundary conditions. Geometry optimizations for the AGNRs were carried out in two steps. In the first step, a constrained geometry optimization maintaining the planarity of the structure was performed at the zeroth-order DFTB level for an electronic temperature of 0 K. In the second step, the output geometry was supplied as input for another constrained geometry optimization at 50 K using second-order DFTB. The self-consistency criterion was set to  $10^{-5}$  e. In both cases the residual force on each atom was smaller than  $10^{-4}$  a.u.

Next, the electronic ground state was determined for the optimized structures. To this end spinrestricted singlet (unpolarized, UP), biradical singlet (anti-ferromagnetic, AF) as well as triplet (T) calculations were performed using a self-consistency criterion of  $10^{-8}$  e at 0 K. In order to break spin symmetry a proper spin initialization on the carbon atoms belonging to the edge of the AGNR is required. The left and right edges of the AGNRs were determined by identifying the central repeating unit. The carbon atoms belonging to this unit were neglected and the remaining structure belonged to the left or the right edge. The biradical singlet state was then initialized by alternating spins on edge carbon atoms. The Fortran code that was used for this purpose (find\_edge\_fp.f90.txt) is given in the supporting material.

Carlos-Andres Palma<sup>1</sup>, Manohar Awasthi<sup>2</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A. Niehaus<sup>2</sup> and Johannes V. Barth<sup>11</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany <sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Additionally, first principles DFT calculations using the ADF package<sup>8</sup> were performed on five randomly chosen AGNRs. We considered the local LDA<sup>9</sup>, the gradient-corrected PBE<sup>10</sup> and the hybrid B3LYP<sup>11</sup> exchange-correlation functional with a triple-zeta polarized basis set (TZP). Input geometry and spin initialization were taken as in the DFTB case.

## 2. Geometrical and energetic analysis of selected models



**Figure S1** Geometries for chosen molecules of families 3a, 3b, 3c, after second-order DFTB relaxation to  $<10^{-4}$  a.u force per atom at 50 K. Before optimization, every C-C bond is set to 1.40 Å and the structures are 40.46, 44.65 and 40.46 Å long, respectively. After optimization the structures are 41.50, 45.70 and 41.46 Å long, respectively.



**Figure S2** Unpolarized ground state of 4d (left) compared to the antiferromagnetic ground state of 4c (right) for 48.8 Å long (length calculated before optimization, C-C bonds 1.4Å) structures. The inset depicts the structures' HOMO after geometrical relaxation.

Carlos-Andres Palma<sup>1</sup>, Manohar Awasthi<sup>2</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A. Niehaus<sup>2</sup> and Johannes V. Barth<sup>11</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany <sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

# 3. Method validation for selected models

**Table S1** Total energies [eV] with respect to the electronic ground state for selected model compounds (depicted below) at different levels of theory as explained in the method section. The term NC indicates that the DFTB calculation did not converge at T = 0 K.

Configuration	LDA	PBE	B3LYP	DFTB
Model 1 (9-AGNR)				
AF	0.0000	0.0000	0.0000	0.0000
Т	0.0005	0.0010	0.0045	0.0066
UP	0.1060	0.1647	0.5688	0.0362
Model 2 (5-AGNR)				
AF	0.0000	0.0000	0.0000	0.0000
Т	0.0045	0.0031	0.0032	0.0015
UP	0.1136	0.1952	0.6841	0.0848
Model 3 (9-AGNR)				
UP	0.0000	0.0000	0.0000	0.0000
AF	0.0000	0.0000	0.0000	0.0000
Т	1.0152	0.9968	1.1522	1.1353
Model 4 (6-AGNR)				
UP	0.0000	0.0000	0.0000	0.0000
AF	0.0000	0.0000	0.0000	0.0000
Т	1.3360	1.3214	1.5593	1.4594
Model 5 (5-AGNR)				
Т	0.0000	0.0000	0.0000	0.0000
AF	0.7689	0.0227	0.0468	0.0108
UP	0.1227	1.2407	0.5400	NC



**Figure S3** Spin density (difference between the densities of spin up and spin down electrons) at the B3LYP/TZVP level for Model 1. The ground state is anti-ferromagnetic.

Carlos-Andres Palma<sup>1</sup>, Manohar Awasthi<sup>2</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A. Niehaus<sup>2</sup> and Johannes V. Barth<sup>11</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany <sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany



Figure S4 Spin density at the B3LYP/TZVP level for Model 2. The ground state is anti-ferromagnetic.



**Figure S5** HOMO of Model 3 at the B3LYP/TZVP level. The ground state is an unpolarized singlet state with zero spin density.



**Figure S6** HOMO of Model 4 at the B3LYP/TZVP level. The ground state is an unpolarized singlet state with zero spin density.

Carlos-Andres Palma<sup>1</sup>, Manohar Awasthi<sup>2</sup>, Yenny Hernandez<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Thomas A. Niehaus<sup>2</sup> and Johannes V. Barth<sup>11</sup>Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany <sup>2</sup>Institute I - Theoretical Physics, University of Regensburg, D-93040 Regensburg, Germany <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany



Figure S7 Spin density at the B3LYP/TZVP level for Model 5. The ground state is a triplet.

# REFERENCES

(1) Elstner, M.; Seifert, G. Density Functional Tight Binding. *Philos. Trans. R. Soc., A* **2014,** *372*, 20120483.

(2) Aradi, B.; Hourahine, B.; Frauenheim, T. Dftb+, a Sparse Matrix-Based Implementation of the Dftb Method. *J. Phys. Chem. A* **2007**, *111*, 5678-5684.

(3) Krüger, T.; Elstner, M.; Schiffels, P.; Frauenheim, T. Validation of the Density-Functional Based Tight-Binding Approximation Method for the Calculation of Reaction Energies and Other Data. . *Chem. Phys.* **2005**, *122*.

(4) Otte, N.; Scholten, M.; Thiel, W. Looking at Self-Consistent-Charge Density Functional Tight Binding from a Semiempirical Perspective. *J. Phys. Chem. A* **2007**, *111*, 5751-5755.

(5) Zheng, G. S.; Lundberg, M.; Jakowski, J.; Vreven, T.; Frisch, M. J.; Morokuma, K. Implementation and Benchmark Tests of the Dftb Method and Its Application in the Oniom Method. *Intl. J. Quantum Chem.* **2009**, *109*, 1841-1854.

(6) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. Self-Consistent-Charge Density-Functional Tight-Binding Method for Simulations of Complex Materials Properties. *Phys. Rev. B* **1998**, *58*, 7260-7268.

(7) Porezag, D.; Frauenheim, T.; Kohler, T.; Seifert, G.; Kaschner, R. Construction of Tight-Binding-Like Potentials on the Basis of Density-Functional Theory - Application to Carbon. *Phys. Rev. B.* **1995**, *51*, 12947-12957.

(8) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with Adf. *J. Comp. Chem.* **2001**, *22*, 931-967.

(9) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin-Density Calculations - a Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200-1211.

(10) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

(11) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab-Initio Calculation of Vibrational Absorption and Circular-Dichroism Spectra Using Density-Functional Force-Fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627.