Title: “Functionalization of two-dimensional phthalo-carbonitride with metal atoms”
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Supplementary Information

I. Comparison of results with different pseudopotentials and exchange-correlation functionals

In Figs. 1-4 we compare the electronic densities of states for the two-dimensional (2D) materials studied here as obtained by different methods. In the following, US (MT) refers to ultrasoft [1] (norm-conserving [2] Martins-Troullier) pseudopotentials, whereas PW (PBE) refers to the Perdew-Wang [3] (Perdew-Burke-Ernzerhof [4]) exchange-correlation functional. Overall, there are small differences between the Zn- and Cu-related results of the two approaches, whereas the Al-related results of the two sets of calculations essentially coincide.

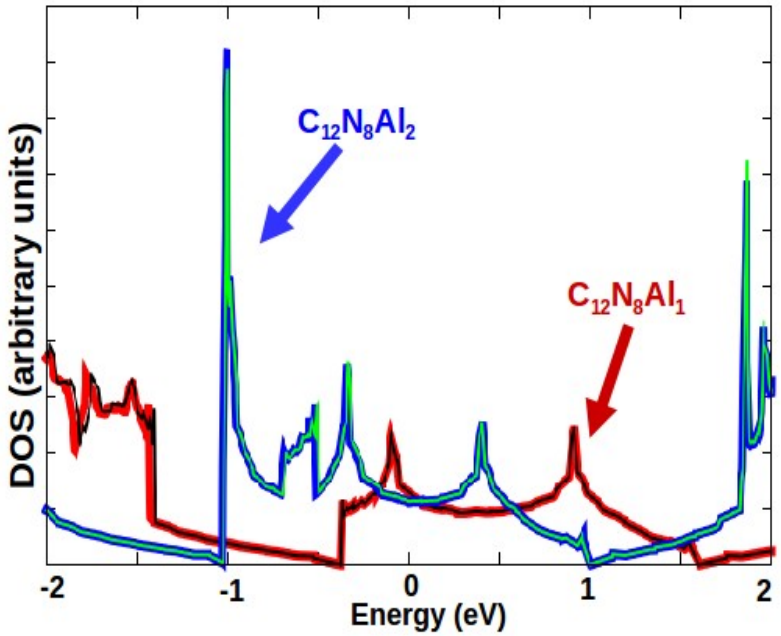

Figure 1: Electronic density of states (DOS) for a phthalo-carbonitride (pc-C_3N_2) layer with one (composition $C_{12}N_8Al_1$, black line for US-PW, red line for MT-PBE) or two (composition $C_{12}N_8Al_2$, green line for US-PW, blue line for MT-PBE) Al atoms in the unit cell. Zero of energy is set at the Fermi level.

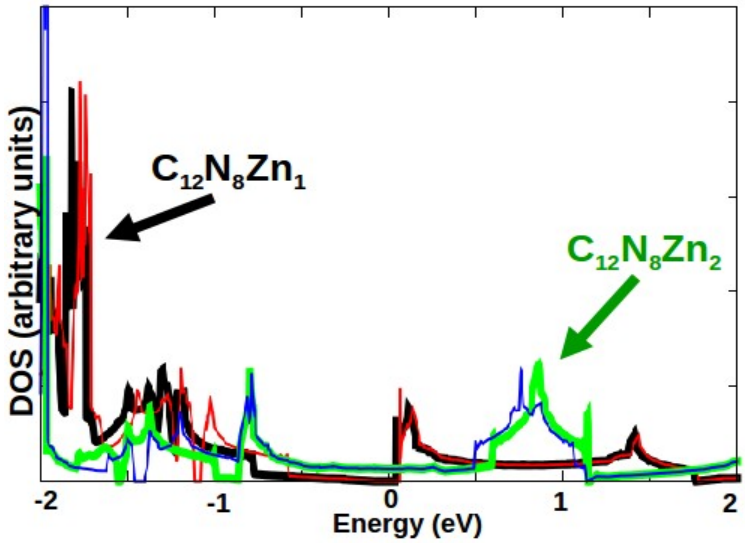

Figure 2: Electronic density of states (DOS) for a phthalo-carbonitride (pc-C_3N_2) layer with one (composition $C_{12}N_8Zn_1$, black line for US-PW, red line for MT-PBE) or two (composition $C_{12}N_8Zn_2$, green line for US-PW, blue line for MT-PBE) Al atoms in the unit cell. Zero of energy is set at the Fermi level.

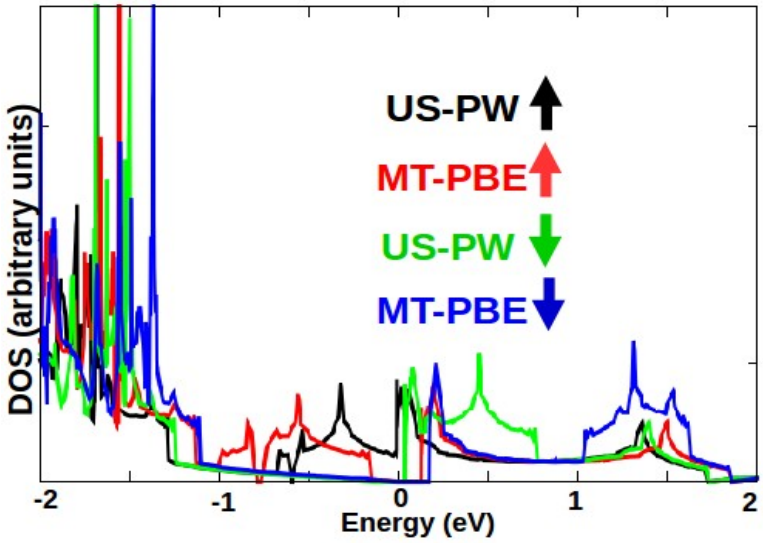

Figure 3: Electronic density of states (DOS) for a phthalo-carbonitride (pc-C_3N_2) layer with one (composition $C_{12}N_8Cu_1$) Cu atom in the unit cell. The arrows indicate the spin character (up for majority, down for minority). Zero of energy is set at the Fermi level.

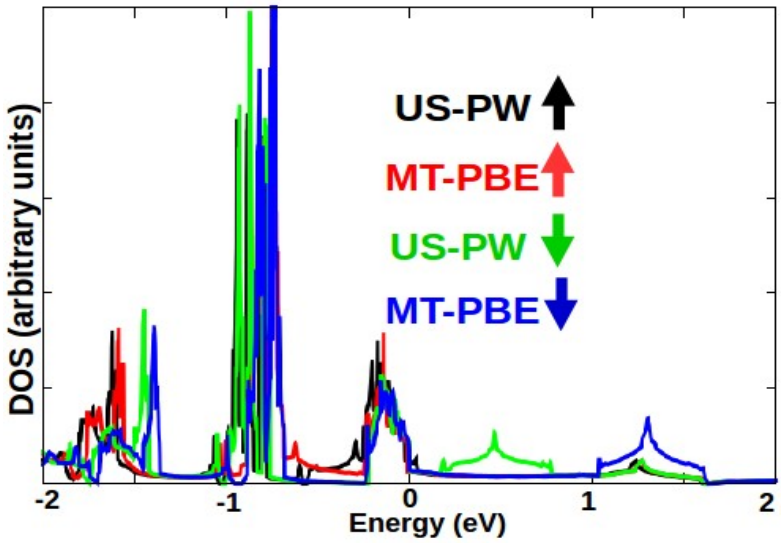

Figure 4: Electronic density of states (DOS) for a phthalo-carbonitride (pc-C_3N_2) layer with two (composition $C_{12}N_8Cu_2$) Cu atoms in the unit cell. The arrows indicate the spin character (up for majority, down for minority). Zero of energy is set at the Fermi level.

II. Electron Localization Function and Charge Density

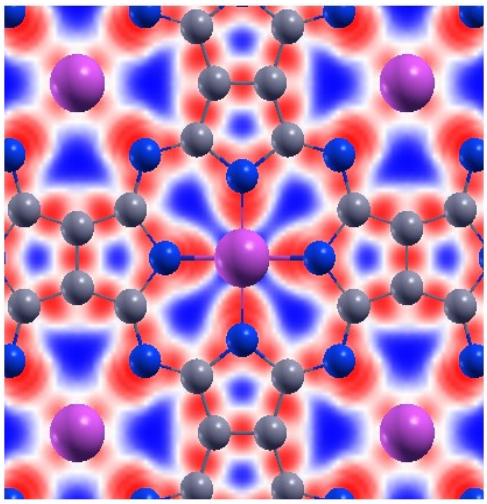

Figure 5: Plot of the Electron Localization Function (ELF) [5] in the plane of the S1 structure of $C_{12}N_8Al_2$. ELF values increase from blue to white to red. The red areas show covalent bonds of the following type: C-C (strong), C-N (strong), N-Al at H1 site (strong), N-Al at H2 site. The latter bonds are not as strong as the other ones. The corresponding N atoms have lone pairs, which give a mixed covalent-polar character to these N-Al bonds.

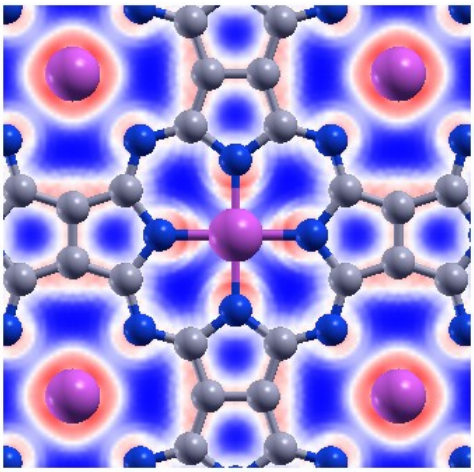

Figure 6: Same as Fig. 5, but for the S2 structure of $C_{12}N_8Al_2$. ELF contours are shown in the plane defined by Al atoms at H2 sites. While N-Al bonds at H1 sites retain their covalent character, N-Al bonding at H2 sites has a stronger polar component compared to similar bonds in the S1 geometry.

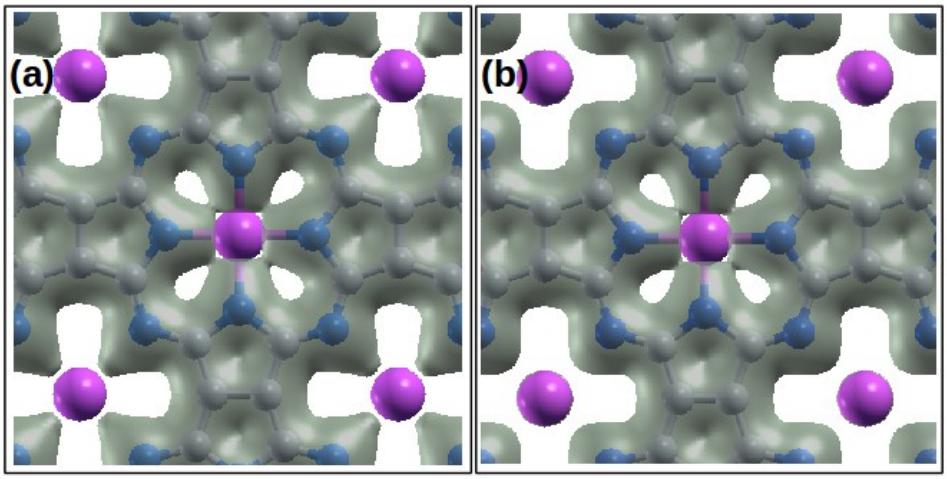

Figure 7: Charge density isosurfaces for (a) the S1 and (b) S2 structures of $C_{12}N_8Al_2$. The same isovalue has been selected to facilitate direct comparison. A depletion of charge can be noticed around the Al atoms of the H2 sites in the S2 configuration, consistent with the stronger polar character of the respective N-Al bonding in this case.

III. Energy band structures

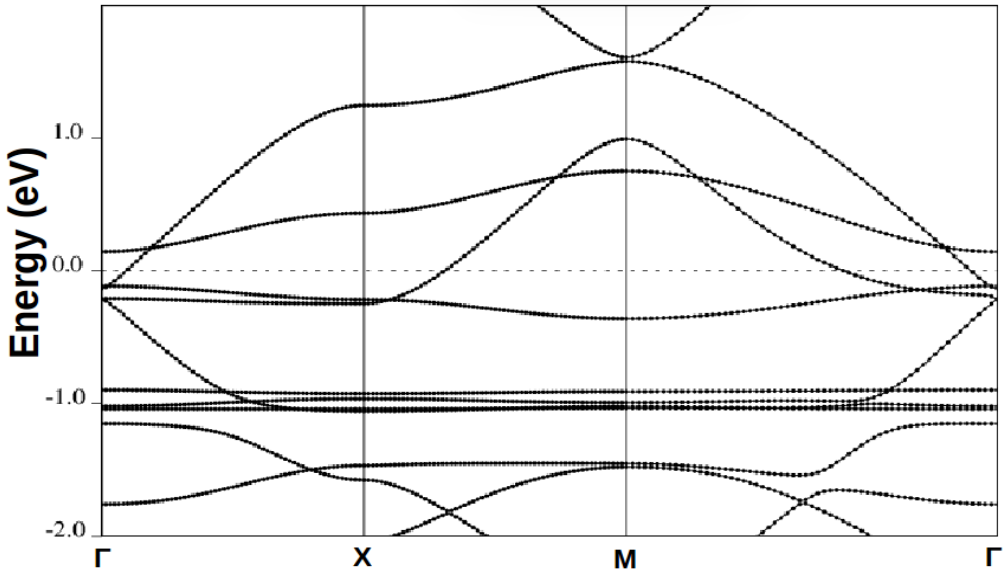

Figure 8: Energy band structure for the majority spin channel of $C_{12}N_8Cu_2$. Zero of energy is set at the Fermi level. X is at the center of a side of the Brillouin zone (BZ), M is one of the corresponding BZ vertices.

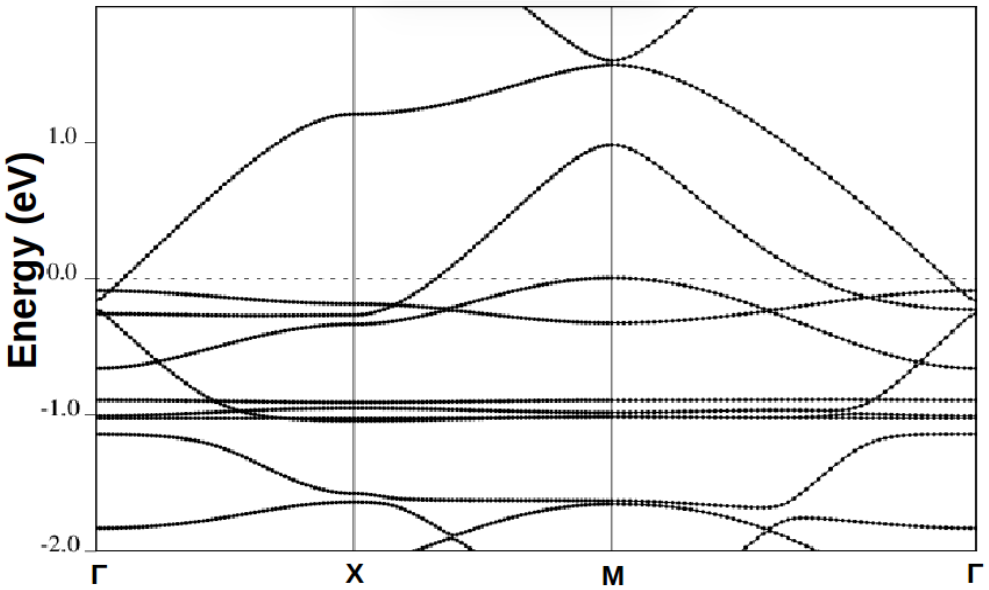

Figure 9: Energy band structure for the minority spin channel of $C_{12}N_8Cu_2$. Zero of energy is set at the Fermi level. X is at the center of a side of the Brillouin zone (BZ), M is one of the corresponding BZ vertices.

IV. Projected densities of states (PDOS)

All PDOS were calculated with Gaussian smearing.

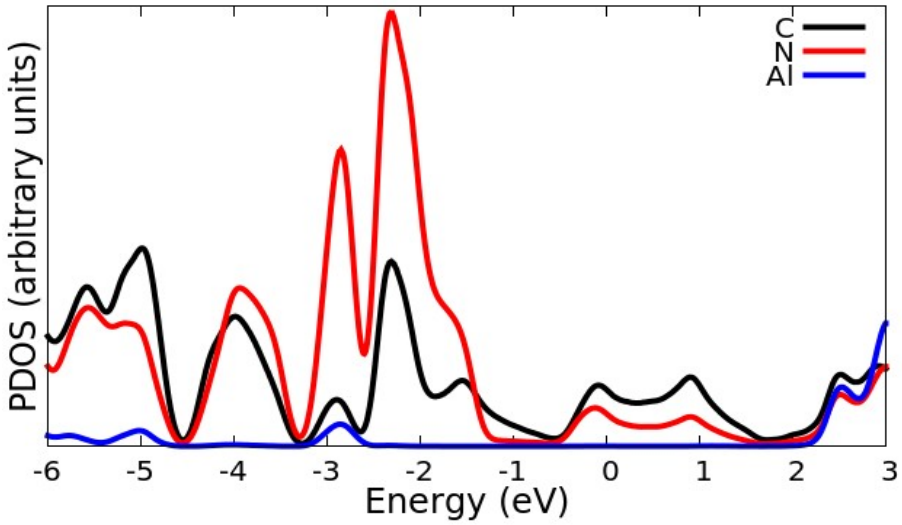

Figure 10: Projected densities of states for $C_{12}N_8Al_1$: black line for the set of C atoms, red line for the set of N atoms, blue line for the Al atom at the H1 site. Zero of energy is set at the Fermi level. C- and N-related states dominate close to the Fermi energy, the Al atom has a significant contribution about 3 eV below and above 2 eV with respect to the Fermi level.

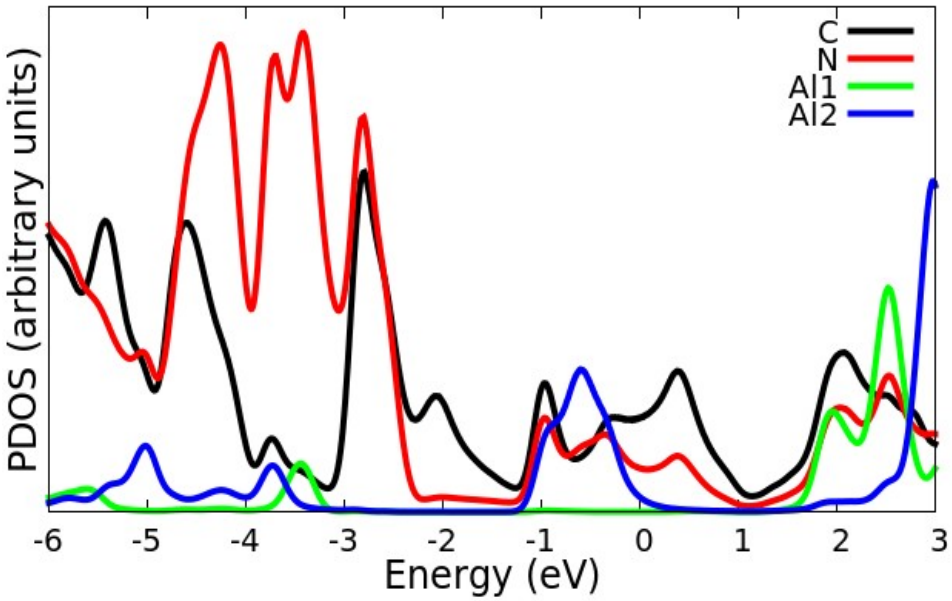

Figure 11: Projected densities of states for $C_{12}N_8Al_2$: black line for the set of C atoms, red line for the set of N atoms, green line for the Al atom (Al1) at the H1 site, blue line for the Al atom (Al2) at the H2 site. Zero of energy is set at the Fermi level. The Al2 atom has a significant contribution just below the Fermi energy.

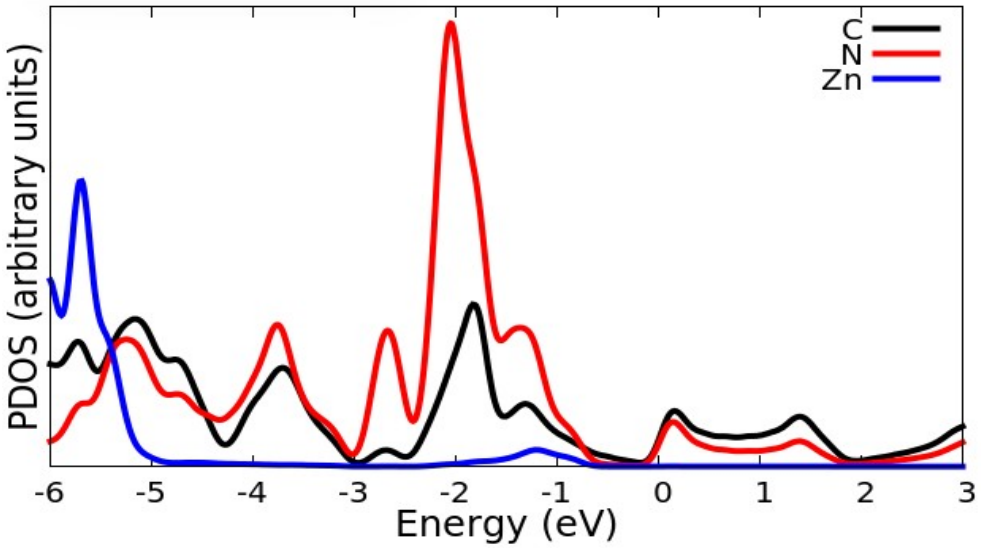

Figure 12: Projected densities of states for $C_{12}N_8Zn_1$: black line for the set of C atoms, red line for the set of N atoms, blue line for the Zn atom at the H1 site. Zero of energy is set at the Fermi level. C- and N-related states dominate close to the Fermi energy, the Zn atom has a significant contribution about 1 eV below the Fermi level.

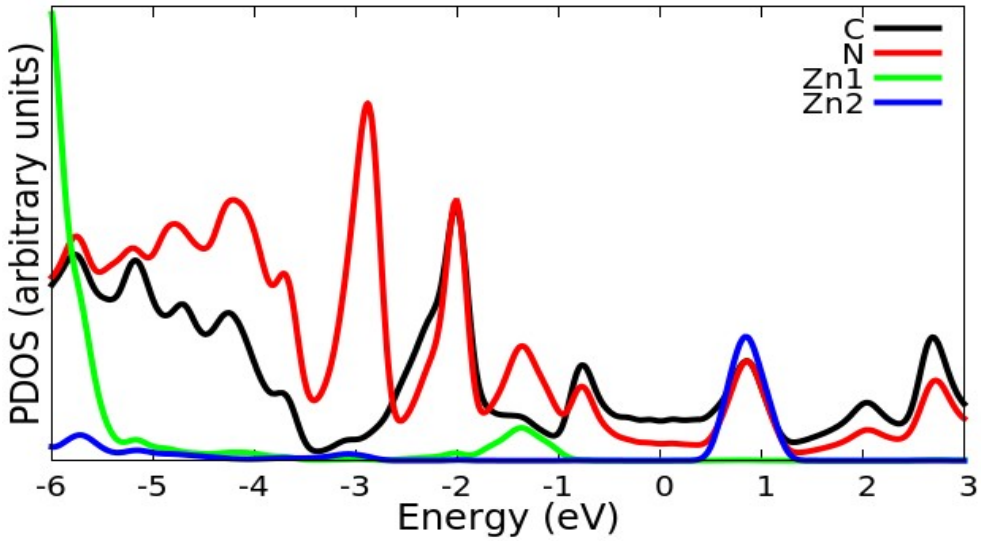

Figure 13: Projected densities of states for $C_{12}N_8Zn_2$: black line for the set of C atoms, red line for the set of N atoms, green line for the Zn atom (Zn1) at the H1 site, blue line for the Zn atom (Zn2) at the H2 site. Zero of energy is set at the Fermi level. The Zn1 (Zn2) atom has a significant contribution about 1.5 eV below (1 eV above) the Fermi energy.

V. Structural details of Zn- and Cu-functionalized pc-C3N2

The attached c3n2.cu02.S3.xyz and c3n2.zn02.S3.xyz files give the coordinates of all atoms (in xyz format) for the S3 geometries of $C_{12}N_8Cu_2$ and $C_{12}N_8Zn_2$.

References

[1] D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892.
[2] N. Troullier and J. L. Martins, *Phys. Rev. B*, 1991, **43**, 1993.
[3] J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.
[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
[5] B. Silvi and A. Savin, *Nature*, 1994, **371**, 683.