

Supporting Information

for

$[(\eta^2-(\text{Si/Ge})_4)\text{Zn}(\eta^2-(\text{Si/Ge})_4)]^{6-}$ - Novel Zintl Clusters with Mixed Si/Ge Tetrahedra bridged by a Zn Atom

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Experimental Details:

All manipulations were carried out under argon atmosphere using standard Schlenk and glovebox techniques. Ph_2Zn (Ph = phenyl, 99%, ABCR) was used as received. [18]-crown-6 was sublimated under dynamic vacuum at 80 °C. [2.2.2]crypt was dried *in vacuo*. Liquid ammonia was dried and stored over sodium metal. Si powder (99.9999%, AlfaAesar) and Ge pieces (99.999%, Chempur) were used as received, K was purified by liquating.

X-ray powder diffraction: Phase analyses of $\text{K}_{12}\text{Si}_{12}\text{Ge}_5$ was performed using a Stoe STADI P diffractometer (Ge(111) monochromator; $\text{Cu}_{\text{K}\alpha 1}$ radiation) equipped with a linear position-sensitive detector. For sample preparation the products were finely ground in an agate mortar, mixed with diamond powder and filled into sealed glass capillaries. The samples were measured in Debye-Scherrer mode ($2\theta_{\text{max}} = 90^\circ$). Data analysis was carried out using the Stoe WinXPOW software package.¹

Single-crystal structure determination: The thermally very unstable, air- and moisture-sensitive crystals of **1** and **2** were transferred from the reaction mixture into perfluoropolyalkyl ether oil at 213 K under a cold N_2 stream. The single crystals were fixed on a glass capillary and positioned in a 120 K cold N_2 stream using the crystal cap system. The data collection was performed at 120(2) K using an Oxford-Diffraction Xcalibur3 diffractometer ($\text{Mo}_{\text{K}\alpha}$ radiation). Structures were solved by Direct Methods (SHELXS-97)² and refined by full-matrix least-squares calculations

against F^2 (SHELXL-97).³ CCDC-876865 and CCDC-876866 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

EDX analysis of the crystals of **1** and **2** was carried out on a JEOL-SEM 5900LV spectrometer equipped with an Oxford Instruments INCA energy dispersive X-ray microanalysis system.

The ternary Zintl phase $K_{12}Si_{17-x}Ge_x$ ($x = 5$) was synthesized from a mixture of 6.52 mmol alkali metal and the corresponding molar ratio of a ball milled Si/Ge alloy in sealed tantalum containers. This mixture was heated to 900 °C, held at that temperature for 10 h, and then slowly cooled down to room temperature with a rate of 0.5 K/min.

Compound **1**: $K_{12}Si_{12}Ge_5$ (88 mg; 0.075 mmol), [2.2.2]crypt (51 mg, 0.135 mmol) and Ph_2Zn (17 mg; 0.075 mmol) were weighed into a Schlenk tube and dissolved in approximately 1 mL liquid ammonia at -78 °C. The resulting red reaction mixture, still containing an insoluble, not further characterized residue, was kept at -70 °C. **1** crystallized as dark red plates which were isolated after 14 weeks with low yield. Crystal size: 0.15 x 0.15 x 0.1 mm³; unit cell parameters: $a = 9.0694(5)$ Å, $b = 11.4274(5)$ Å, $c = 15.8894(8)$ Å, $\alpha = 77.468(4)$ °, $\beta = 81.547(4)$ °, $\gamma = 87.070(4)$ °, $V = 1589.8(2)$ Å³; triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $\rho_{calc} = 1.794$ g cm⁻³, $\mu = 4.802$ mm⁻¹, $\theta_{max} = 27.50$ °, 14501 measured reflections, 7193 independent reflections, $R_{int} = 0.059$, $R_1 = 0.041$ and $wR_2 = 0.079$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.090$ and $wR_2 = 0.086$ for all data. EDX analysis confirmed the presence of Zn, Si, Ge and K in single crystals of **1**. Observed ratio for Zn/Si/Ge/K: 6(2)/34(4)/19(5)/41(4) atom-%.

Compound **2**: $K_{12}Si_{12}Ge_5$ (88 mg; 0.075 mmol), [18]-crown-6 (36 mg, 0.135 mmol) and Ph_2Zn (17 mg; 0.075 mmol) were weighed into a Schlenk tube and dissolved in approximately 1 mL liquid ammonia at -78 °C. The resulting red solution, still containing an insoluble, not further characterized residue, was kept at -70 °C. **2** crystallized as red plates which were isolated after 16 weeks with low yield. Crystal size: 0.2 x 0.15 x 0.1 mm³; unit cell parameters: $a = 9.5430(3)$ Å, $b = 12.2351(4)$ Å, $c = 13.8927(4)$ Å, $\beta = 103.145(3)$ °, $V = 1579.60(8)$ Å³; monoclinic, space group $P2_1$ (No. 4), $Z = 2$, $\rho_{calc} = 1.858$ g cm⁻³, $\mu = 5.334$ mm⁻¹, $\theta_{max} = 26.25$ °, 12970 measured reflections, 5149 independent reflections, $R_{int} = 0.055$, $R_1 = 0.036$ and $wR_2 = 0.075$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.066$ and $wR_2 = 0.079$ for all data. $BASF = 0.55(3)$. EDX analysis confirmed the presence of Zn, Si, Ge and K in single crystals of **2**. Observed ratio for Zn/Si/Ge/K: 7(2)/44(5)/6(2)/43(5) atom-%.

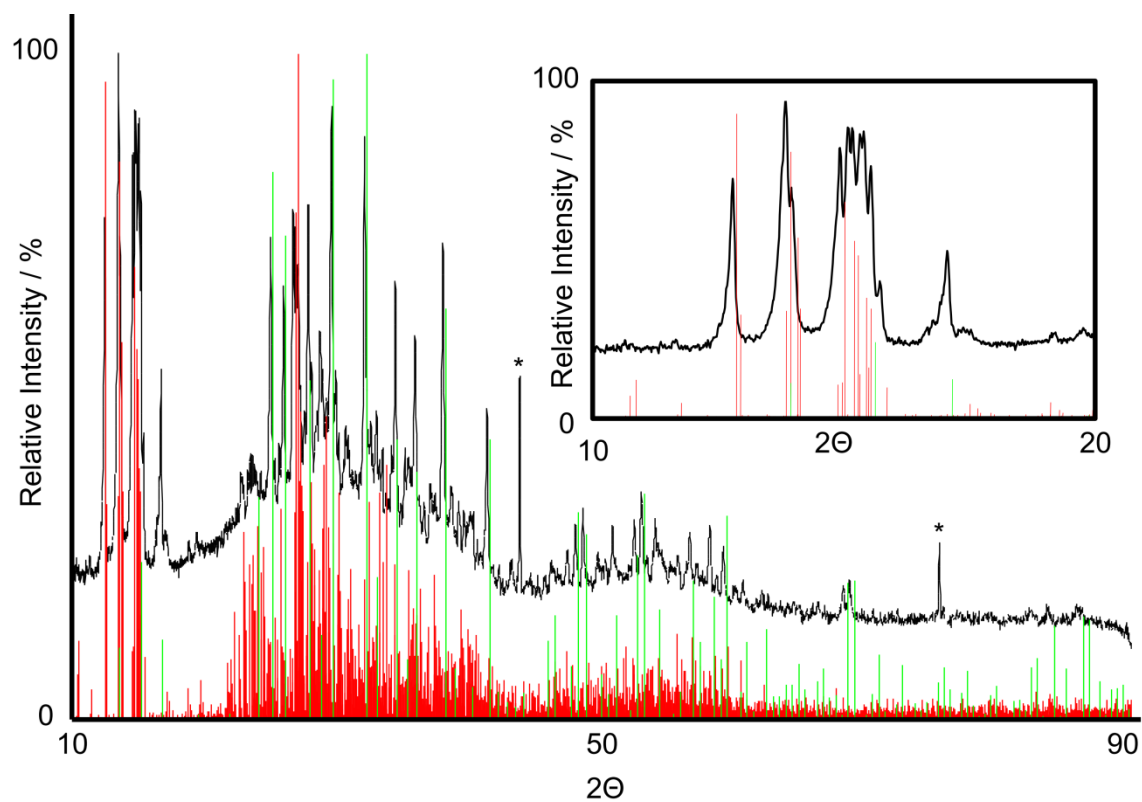


Figure S1: X-ray powder diagram of $K_{12}Si_{12}Ge_5$ ($2\theta = 10 - 90^\circ$) with the smaller picture showing an enlarged section ($2\theta = 10 - 20^\circ$). Theoretical powder diagram of $K_{12}Si_{17}$ colored in red. The theoretical diagram for KSi is colored in green. The reflections resulting from the diamond powder are marked with *.

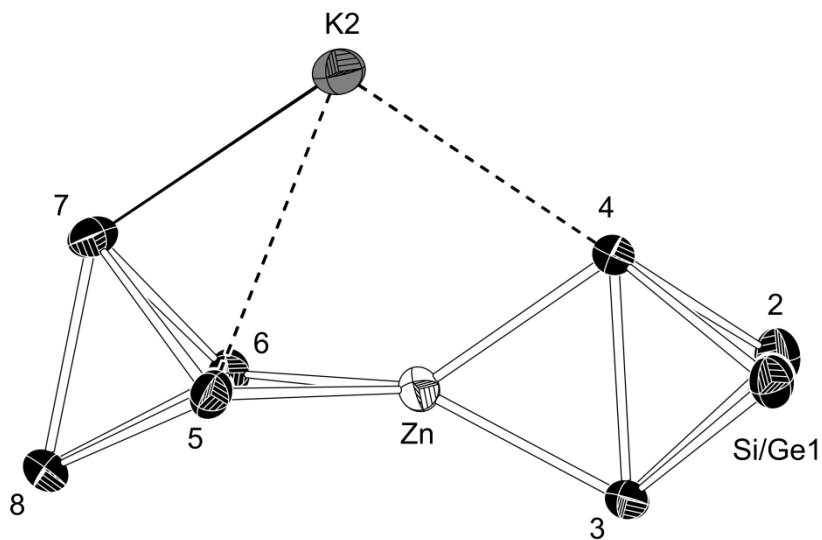


Figure S2: Structure of the novel dimeric tetrahedral Zintl cluster $[(\eta^2-E_4)Zn(\eta^2-E_4)]^{6-}$ (**1a**). Displacement ellipsoids are drawn at the 70% probability level. Si amounts at atomic sites *E* in % (standard deviation): *E*1 37.9(4), *E*2 39.5(4), *E*3 78.5(4), *E*4 72.8(4), *E*5 68.3(4), *E*6 82.4(4), *E*7 53.9(4), *E*8 36.9(4). Selected bond lengths / Å: *E*1 - *E*2 = 2.564(1), *E*1 - *E*3 = 2.471(2), *E*1 - *E*4 = 2.457(1), *E*2 - *E*3 = 2.452(1), *E*2 - *E*4 = 2.471(1), *E*3 - *E*4 = 2.621(2), Zn - *E*3 = 2.509(1), Zn - *E*4 = 2.535(1), Zn - *E*5 = 2.545(1), Zn - *E*6 = 2.468(1), *E*5 - *E*6 = 2.640(2), *E*5 - *E*7 = 2.459(1), *E*5 - *E*8 = 2.483(1), *E*7 - *E*8 = 2.549(1), *E*6 - *E*7 = 2.450(2), *E*6 - *E*8 = 2.449(1), K2 - *E*7 = 3.292(2). K - *E* distances longer than 3.4 Å are shown as dotted lines.

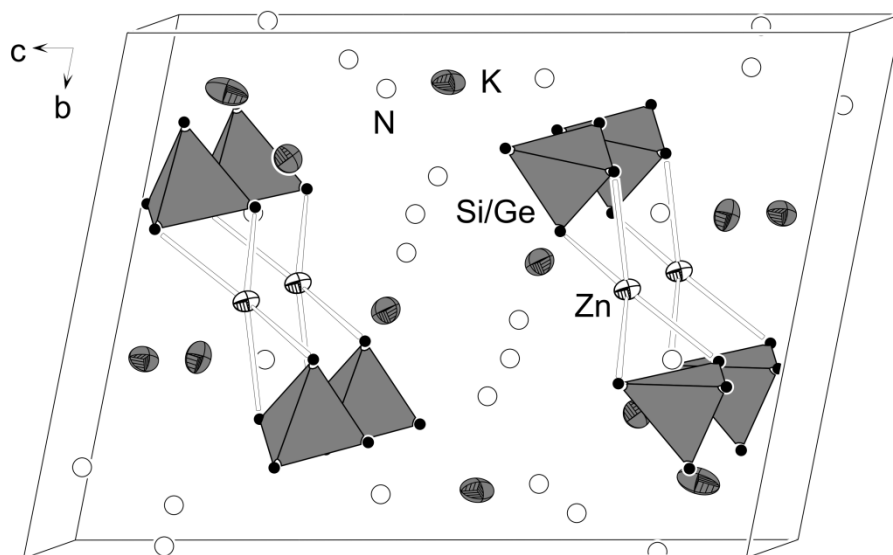


Figure S3a: Unit cell of **1** (triclinic space group $P\bar{1}$; view along the crystallographic [100] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70 % probability. Ammonia molecules are schematically shown for clarity.

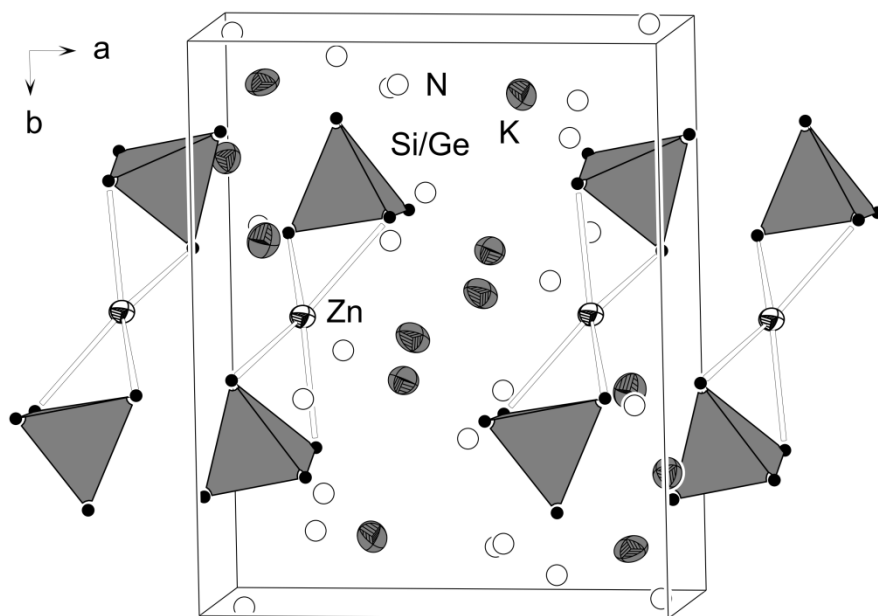


Figure S3b: Unit cell of **1** (triclinic space group $P\bar{1}$; view along the crystallographic [001] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70 % probability. Ammonia molecules are schematically shown for clarity.

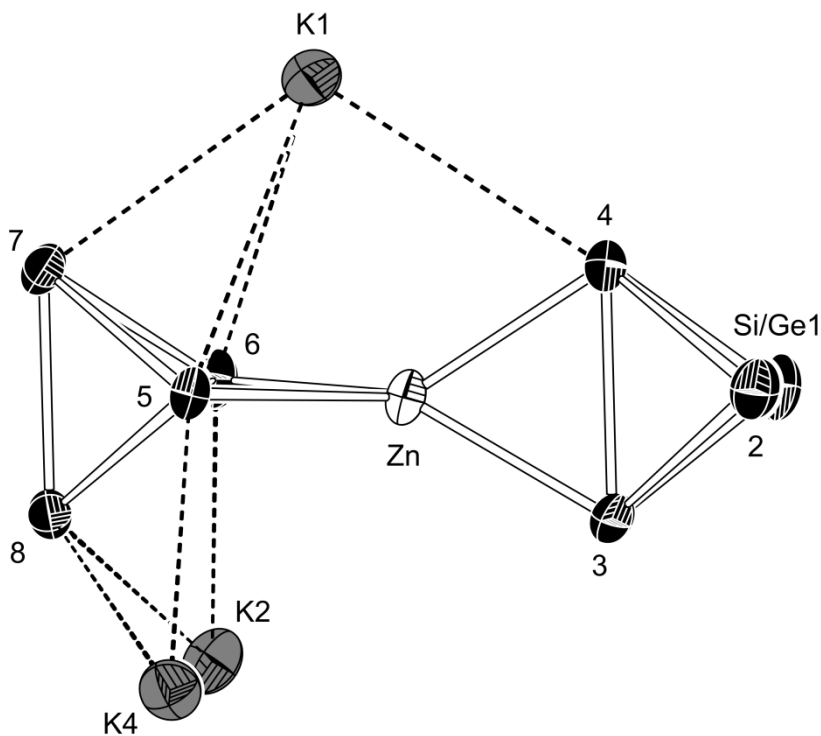


Figure S4: Structure of the novel dimeric tetrahedral Zintl cluster $[(\eta^2-E_4)Zn(\eta^2-E_4)]^{6-}$ (**2a**). Displacement ellipsoids are drawn at the 70% probability level. Si amounts at atomic sites *E* in % (standard deviation): *E1* 30.5(9), *E2* 32.9(9), *E3* 63.6(5), *E4* 71.8(5), *E5* 70.8(8), *E6* 75.1(8), *E7* 38.2(5), *E8* 31.9(5). Selected bond lengths / Å: *E1* - *E2* = 2.549(1), *E1* - *E3* = 2.481(3), *E1* - *E4* = 2.467(3), *E2* - *E3* = 2.465(3), *E2* - *E4* = 2.478(2), *E3* - *E4* = 2.639(2), Zn - *E3* = 2.510(1), Zn - *E4* = 2.511(2), Zn - *E5* = 2.494(3), Zn - *E6* = 2.516(3), *E5* - *E6* = 2.622(2), *E5* - *E7* = 2.457(3), *E5* - *E8* = 2.475(3), *E7* - *E8* = 2.572(1), *E6* - *E7* = 2.449(3), *E6* - *E8* = 2.484(3). K - *E* distances longer than 3.4 Å are shown as dotted lines.

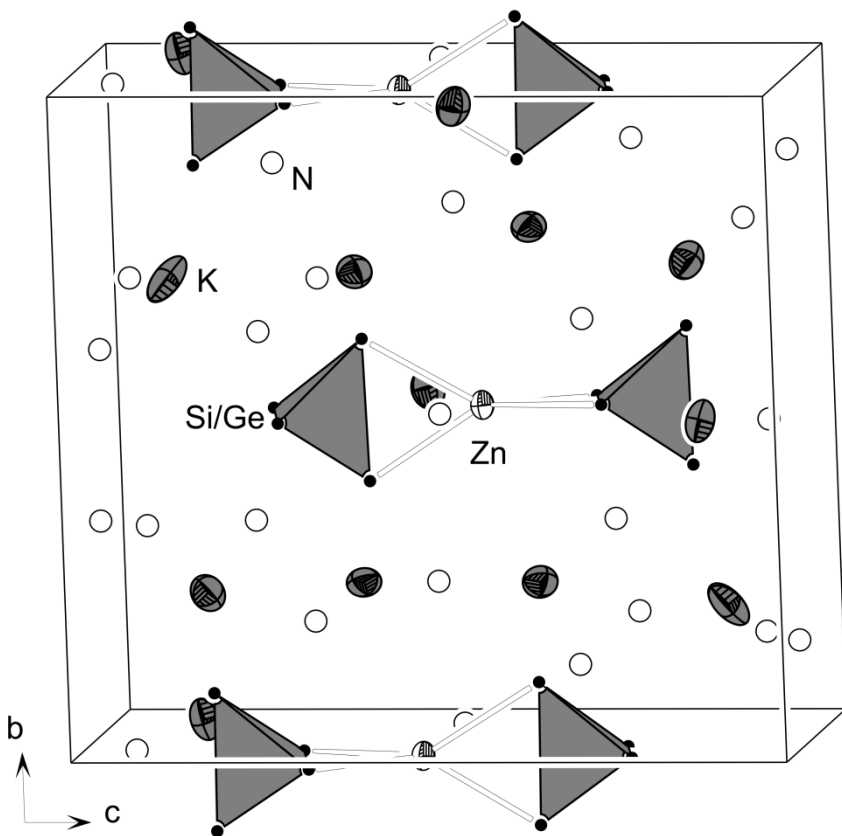


Figure S5: Unit cell of **2** (monoclinic space group $P2_1$; view along the crystallographic [100] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70 % probability. Ammonia molecules are schematically shown for clarity.

Computational Details:

DFT-calculations on $[\text{Si}_4]^{4-}$, $[\text{Si}_2\text{Ge}_2]^{4-}$ and $[\text{Ge}_4]^{4-}$ were performed in the Gaussian09. program package.⁴ For all calculations the exchange correlation hybrid functional after Perdew, Burke, and Ernzerhof (PBE0)^{5,6} was used together with triple-zeta-valence + polarization quality basis set (Def2-TZVP).⁷ For compensation of the negative cluster charges, a solvation model (Polarizable Continuum Model, PCM) was used. Harmonic vibration frequencies were calculated to characterize the nature of the stationary point on the potential energy surface.

Table S1: Comparison of electronic and Gibbs free energy for two possibilities of mixing the clusters according to Scheme S1. The differences of their absolute total energies Δ_E and Gibbs free energies Δ_G are listed in kJ/mol.

	$\Delta_E/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_G/\text{kJ}\cdot\text{mol}^{-1}$
$[\text{Si}_4]^{4-} + [\text{Ge}_4]^{4-}$	1.0	4.6
$2 [\text{Si}_2\text{Ge}_2]^{4-}$	0	0

Scheme S1:

The HOMO-LUMO gap of the mixed cluster $[\text{Si}_2\text{Ge}_2]^{4-}$ is very close to the $[\text{Si}_4]^{4-}$ tetrahedron (Table S2). Additionally the difference to $[\text{Ge}_4]^{4-}$ is very small (range from 4.04 eV to 4.49 eV).

Table S2: HOMO-LUMO gaps for the homoatomic and the mixed $[\text{Si}_2\text{Ge}_2]^{4-}$ tetrahedral clusters formed of Si and Ge, calculated with Gaussian09⁴ after structure optimization.

Compound	gap /eV
$[\text{Si}_4]^{4-}$	4.05
$[\text{Si}_2\text{Ge}_2]^{4-}$	4.04
$[\text{Ge}_4]^{4-}$	4.29

Table S3: Comparison of resulting bond lengths in molecular $[\text{Si}_4]^{4-}$, $[\text{Si}_2\text{Ge}_2]^{4-}$ and $[\text{Ge}_4]^{4-}$ clusters after their structure optimization with Gaussian09, using the functional PBE0 and def2-TZVP type basis sets for all elements. Bond length differences d are given in percent.

	$d_{\text{Si-Si}}/\text{Å}$	$d_{\text{relat.}}$	$d_{\text{Si-Ge}}/\text{Å}$	$d_{\text{relat.}}$	$d_{\text{Ge-Ge}}/\text{Å}$	$d_{\text{relat.}}$
$[\text{Si}_4]^{4-}$	2.429	1	–	–	–	–
$[\text{Si}_2\text{Ge}_2]^{4-}$	2.424	1.00	2.513	1.04	2.569	1.06
$[\text{Ge}_4]^{4-}$	–	–	–	–	2.580	1.06

Literature:

- (1) WinXPow *Stoe & Cie GmbH, Version 2.08. 2003.*
- (2) Sheldrick, G. M. *SHELXS-97; Program for the Solution of Crystal Structures; Universität Göttingen 1997.*
- (3) Sheldrick, G. M. *SHELXS-97; Program for the Refinement of Crystal Structures; Universität Göttingen 1997.*
- (4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.*
- (5) Perdew, P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (6) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
- (7) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.