CORA Cork Open Research Archive
Cartlann Taighde Oscailte Chorcaí

Title	Engineering the optical response of the titanium-MIL-125 metal-organic framework through ligand functionalization
Authors	Hendon, Christopher H.;Tiana, Davide;Fontecave, Marc;Sanchez, Clement;D'arras, Loic;Sassoye, Capucine;Rozes, Laurence;Mellot-Draznieks, Caroline;Walsh, Aron
Publication date	2013-07-10
Original Citation	Hendon, C. H., Tiana, D., Fontecave, M., Sanchez, C., D'arras, L., Sassoye, C., Rozes, L., Mellot-Draznieks, C. and Walsh, A. (2013) 'Engineering the Optical Response of the Titanium-MIL-125 Metal–Organic Framework through Ligand Functionalization', Journal of the American Chemical Society, 135(30), pp. 10942-10945. doi: 10.1021/ja405350u
Type of publication	Article (peer-reviewed)
Link to publisher's version	https://pubs.acs.org/doi/10.1021/ja405350u - 10.1021/ja405350u
Rights	© 2013 American Chemical Society. ACS AuthorChoice - This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes. - https://pubs.acs.org/page/policy/authorchoice_termsofuse.html
Download date	2026-11-01 12:06:22
Item downloaded from	https://hdl.handle.net/10468/6421



University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

SUPPORTING INFORMATION

Engineering the optical response of the titanium-MIL-125 metal-organic framework through ligand functionalisation

Christopher H. Hendon,[†] Davide Tiana,[†] Marc Fontecave,[‡] Clément Sanchez,[¶] Loïc D'arras,[¶] Capucine Sassoye,[¶] Laurence Rozes,[*,¶] Caroline Mellot-Draznieks,[*,‡] and Aron Walsh[*,†]

[†]Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

[‡] Laboratoire de Chimie des Processus Biologiques, Collège de France, CNRS FRE 3488, 11 Place Marcelin Berthelot, 75005 Paris, France

[¶]UMR 7574 Laboratoire Chimie de la Matiére Condensée de Paris, UPMC Univ Paris 06 - CNRS, Collège de France, 11 Place Marcelin Berthelot, 75231, Paris Cedex 05, France

E-mail: laurence.rozes@college-de-france.fr; caroline.mellot-draznieks@college-de-france.fr ; a.walsh@bath.ac.uk

S1. Experimental methods

Chemicals were purchased from Sigma-Aldrich and used without further purifications. Nitrogen physisorption measurements were performed on a Belsorp max instrument. Powders were washed three times with DMF to remove residual ligands and degassed at 150°C during 24 hours. Powder diffraction patterns were obtained from a Bruker D8 instrument. SEM snapshots were acquired from a Hitachi S-3400N microscope. UV data were collected on a Cary 5000 instrument.

Synthesis of titanium oxo-cluster **$Ti_8O_8(OOCC(CH_3)_3)_{16}$**: 5 mL of $Ti(O^iPr)_4$ is mixed with 17.5 g of trimethylacétic acid (pivalic acid) in 60 mL of acetonitrile in a closed vessel. This preparation is heated at 120°C during three days. Colorless crystals are obtained, isolated and washed with 3 × 10 mL of acetonitrile.

Synthesis of MIL-125: 0.1 g of $Ti_8O_8(OOCC(CH_3)_3)_{16}$ (47 µmol) is mixed with 125 mg of terephthalic acid (753 µmol) in a mixture of 8 mL of DMF (N,N-dimethylformamide) and 2 mL of methanol. This mixture is heated in solvothermal conditions at 150°C during 3 days. A white powder is obtained after centrifugation. The solid is washed by 2 × 10 mL of DMF and 10 mL of methanol and dried at 70°C. Activation of the solid is made by heating the powder in 20 mL of DMF at 150°C during 24 hours, then washing by 10 mL of DMF and 10 mL of methanol and drying at 70°C.

Synthesis with 2-amino terephthalic acid: mixed MIL-125 with terephthalic acid/2-amino terephthalic acid ratio = 90/10: the same procedure is followed with 0.1 g of $Ti_8O_8(OOCC(CH_3)_3)_{16}$ (47 µmol) is mixed with 114 mg of terephthalic acid (688 µmol) and 14 mg of 2-amino terephtalic acid (76 µmol) in a mixture of 8 mL of DMF (N,N-dimethylformamide) and 2 mL of methanol.

Synthesis of mix-MIL-125 with terephthalic acid/2-amino terephhtalic acid ratio = 80/20: The same procedure is followed with 101 mg of terephthalic acid (0.61 mmol) and 28 mg of 2-amino terephthalic acid. (0.15 mmol)

Synthesis of mix-MIL-125 with terephthalic acid/2-amino terephthalic acid ratio = 50/50: The same procedure is followed with 60 mg of terephthalic acid (0.36 mmol) and 66 mg of 2-amino terephthalic acid (0.36 mmol).

Synthesis of MIL-125-NH_2: 0.105 mL of titanium isopropoxide (0.35 mmol) is mixed with 180 mg of 2-amino terephthalic acid (0.98 mmol) in a mixture of 8 mL of DMF (N,N-dimethylformamide) and 2 mL of methanol. The procedure is then identical to those above.

Synthesis with 2,5-diamino terephthalic acid: We tried to synthetize a mixed MIL-125 by combining terephthalic acid and 2,5-diamino terephthalic acid. We reproduced the procedures above and obtained compounds with very poor crystallinity. The modification of the temperature, the time of synthesis, and the amount of the different ligands did not

improve the crystallinity of the products. We also noticed that synthesis done with only 2,5-diamino terephthalic acid led to amorphous compounds. Only synthesis with both mono-aminated and di-aminated ligand led to well crystallized compounds.

Synthesis of mix-MIL-125 with 2-amino terephthalic acid/2,5-diamino terephtalic acid ratio = 90/10: 0.105 mL of titanium isopropoxide (0.35 mmol) is mixed with 163 mg of 2-amino terephthalic acid (0.89 mmol) and 20 mg of 2,5-diamino terephtalic acid (0.1 mmol) in a mixture of 8 mL of DMF (N,N-dimethylformamide) and 2 mL of methanol. The procedure is then identical to those above.

XRD patterns

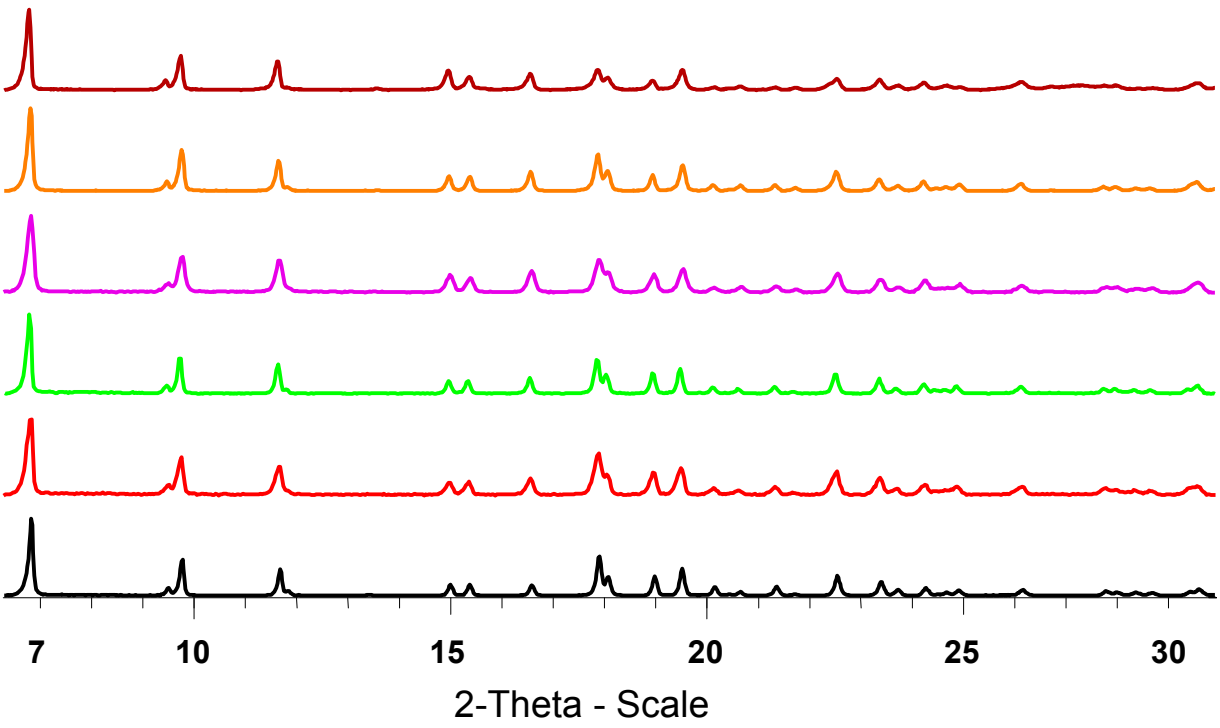


Fig S1: XRD patterns of MIL-125 (black), and mono-aminated bdc-NH_2-based samples: 10%-MIL-125-**NH_2**(red), 20%-MIL-125-**NH_2**(green) 50%-MIL-125-**NH_2**(purple) MIL-125-NH_2 or 100%-MIL-125-**NH_2** (orange) and the 10%/90% di/mono-aminated MIL-125 (brown).

Table S1: Cell parameters for the series of amino-free and aminated MIL-125 solids:

	a (Å)	**c** (Å)
MIL-125	18.693(3)	18.186(3)
10%-MIL125-**NH_2**	18.721(9)	18.21(1)
20%-MIL125-**NH_2**	18.720(4)	18.210(5)
50%-MIL125-**NH_2**	18.71(1)	18.17(1)
100%-MIL125-**NH_2**	18.729(3)	18.172(4)
10%/90%-**di/mono** aminated MIL125	18.697(5)	18.144(5)

The cell parameters have been calculated with Fullprof software using a zero-atom refinement. The following parameters have been allowed to refine: cell parameters, zero shift and peak shape parameters. The zero shift parameters (varied from 0.012 to 0.09) have been implemented into the XRD patterns to draw Fig S1.

Nitrogen sorption

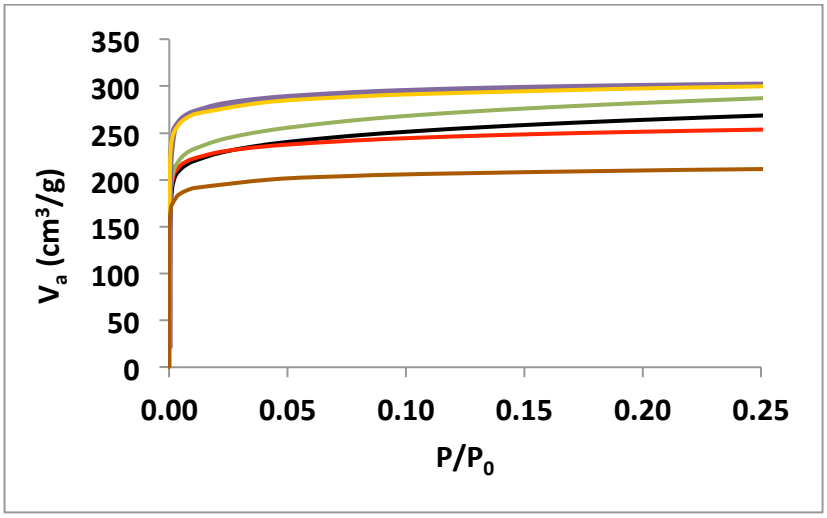


Fig S2: Nitrogen sorption isotherms of the amino-free MIL-125 (black), 10%-MIL-125-**NH_2** (red), 20%-MIL-125-**NH_2** (green), 50%-MIL-125-**NH_2** (purple), MIL-125-**NH_2** (orange) and the 10%/90% di/mono-aminated MIL-125 (brown) performed at 77K. Calculated BET areas are 1080m^2/g, 1000 m^2/g (10%-MIL-125-**NH_2**), 1080 m^2/g (20%-MIL-125-**NH_2**), 1220 m^2/g (50%-MIL-125-**NH_2**) and 1230 m^2/g (MIL-125-**NH_2**)

Optical band gaps

Figure S3-S5 display the UV spectra of the ligand salt and that of the corresponding MIL-125 hybrid solid, i.e. amino-free, with mono-aminated **bdc** and with di-aminated and mono-aminated **bdc**. It reveals that the UV spectrum of the hybrid solid is indeed different from that of the linker's carboxylate salts, as a result of the interaction between the nodal titanium cluster and the organic linker incorporated in the hybrid framework.

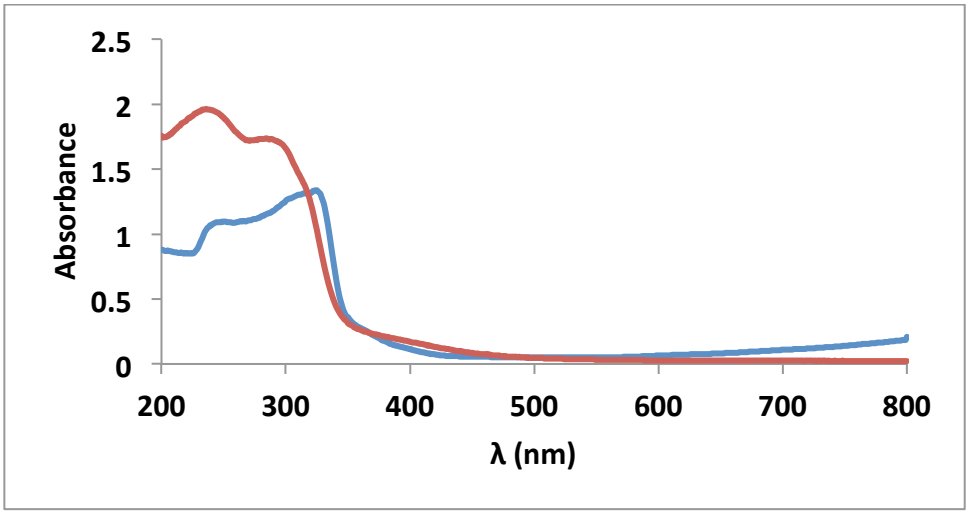


Fig S3: Comparison of UV spectra of **bdc**-MIL-125(Ti) (red) and of the **bdc** linker (blue).

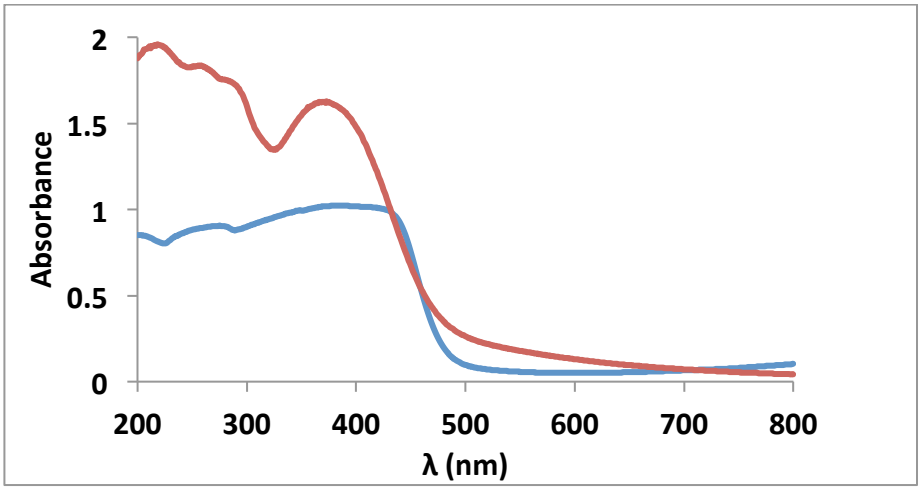


Fig S4: UV spectra of **100%**-MIL-125(Ti)-NH_2 (red) and the **bdc**-NH_2 linker (blue).

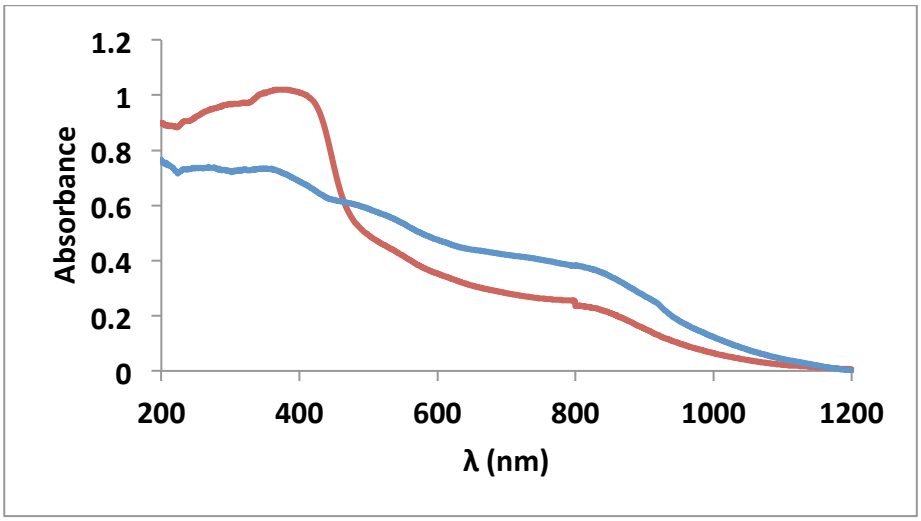


Fig S5: UV spectra of mixed 10% bdc-$(NH_2)_2$/90% bdc-NH_2 MIL-125 (red) and the di-aminated **bdc-$(NH_2)_2$** linker (blue).

Table S2: Optical band gaps measured for the series of amino-free and aminated MIL-125 solids:

% **bcd-NH_2** linker	Gap (eV)
0	3.68 (1)
10%	2.75 (3)
20%	2.55 (2)
50%	2.62 (1)
100%	2.72 (1)
10% **bcd-$(NH_2)_2$** – 90% **bcd-NH_2**	1.23 (2)

These values are obtained by plotting the curve: $(Ahv)^2=f(hv)$. The optical band gaps were calculated under the hypothesis that absorption follows: $(Ahv)^2= \alpha(hv - Eg)$.

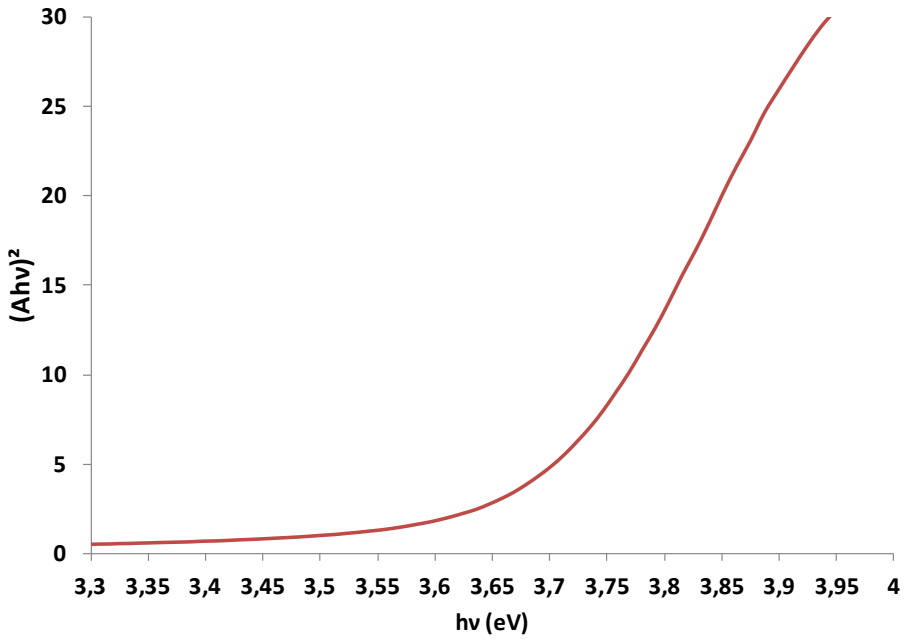


Fig S6: plot of $(Ahv)^2=f(hv)$ for MIL-125

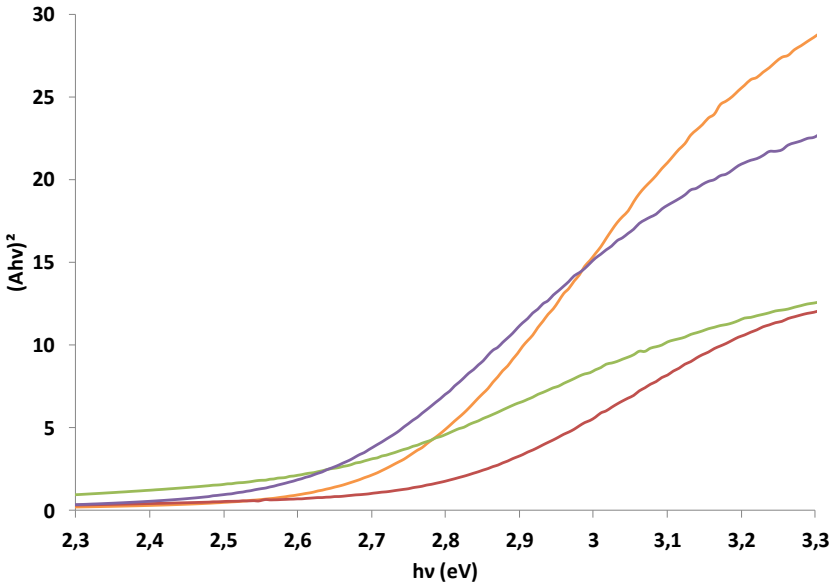


Fig S7: plot of $(Ahv)^2=f(hv)$ for mono-aminated bdc-NH_2-based samples: 10%-MIL-125-**NH_2** (red), 20%-MIL-125-**NH_2** (green) 50%-MIL-125-**NH_2** (purple) MIL-125-NH_2 and 100%-MIL-125-**NH_2** (orange).

S2. Computational methods

All electronic and structural calculations were performed within the Kohn-Sham DFT framework using periodic boundary conditions to approximate the perfect solid. The *Vienna ab initio simulation package* (VASP),[1] a planewave code (with PAW scalar-relativistic pseudopotentials), [2] was employed for all geometry and electronic calculations. Γ-point sampling of the Brillouin zone was used for the un-substituted MIL-125 and for all subsequent derivatives. A 500 eV plane-wave cutoff, for the construction of the electronic wavefunctions, was found to be suitable for convergence of the systems to within 0.01 eV/atom. Starting with the experimentally determined unit cell of MIL-125, both lattice parameters and atomic positions were relaxed with the semi-local Perdew-Burke-Ernzerhof exchange-correlation functional revised for solids (PBEsol).[3] Symmetry of the standard MIL-125 (*I4/mmm*) was enforced in initial relaxation using the crystal structure from Ref 23.

Table S3: Lattice parameter comparison of experimental MIL-125 compared to the structurally relaxed MIL-125.

System	**a**	**b**	**c**
Experimental	19.20845	19.20845	18.18951
Computational	18.92389	18.92389	17.95587

All calculations were performed at the equilibrium MIL-125 geometry, which are within 1.5% of the experiment values. Molecular substitutions were manually installed to the **bdc** motifs, and ionic positions were further relaxed using the same functional. Upon molecular

substitutions the symmetry of the host crystal was broken, and the calculations were performed unconstrained for atomic coordinates. Lattice parameters for the substituted systems were not optimised computationally as the inclusion of the functional groups did not cause a significant increase in the effective cell pressure.

In order to obtain quantitative electronic information, in particular for estimations of the band gaps, hybrid-DFT calculations were performed using the HSE06 functional,[4] with 25% of the short-range semi-local exchange functional replaced by the exact non-local Hartree-Fock exchange. This functional has been shown to perform consistently with inorganic semiconductors as well as hybrid metal-organic materials.[5,6,7,8] Visualizations of the structures and orbitals were made using the codes VESTA and GABEDIT.[9,10]

(1) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, 54, 11169–11186.

(2) Blöchl, P. *Phys. Rev. B* **1994**, 50, 17953–17979.

(3) Perdew, J.; Ruzsinszky, A.; Csonka, G.; Vydrov, O. *Phys. Rev. Lett.* **2008**, 2–6.

(4) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, 118, 8207.

(5) Walsh, A. *J. Phys. Chem. Lett.* **2010**, 1, 1284–1287.

(6) Hummer, K.; Harl, J.; Kresse, G. *Phys. Rev. B* **2009**, 80, 5205.

(7) Kim, Y.-S.; Hummer, K.; Kresse, G. *Phys. Rev. B* **2009** 2009, 80, 1–9.

(8) Wróbel, J.; Kurzydłowski, K.; Hummer, K.; Kresse, G.; Piechota, *J. Phys. Rev. B* **2009**, 80, 1–8.

(9) Momma, K.; Izumi, F. *J. Appl. Cryst.* **2011**, 44, 1272–1276.

(10) Allouche, A. –R. *J. Comput. Chem.* **2010**, 174-182.