Supporting information:

The Predicted Crystal Structure of $Li_4C_6O_6$, an Organic Cathode Material for Li-ion Batteries, from First-Principles Multi-level Computational Methods

Dong-Hwa Seo,[a] Hyungjun Kim,[bc] Haegyeom Kim,[a] William A. Goddard III[bc] and Kisuk Kang*[a]*

[a] Department of Materials Science and Engineering ,Seoul National University

599 Gwanak-ro, Gwanak-gu, Seoul 151-742 (Republic of Korea)

[b] Materials and Process Simulation Center, California Institute of Technology

1200 East California Boulevard, Pasadena, CA 91125 (USA)

[c] Graduate School of EEWS, Korea Advanced Institute of Science Technology

Daejeon, 305-701(Republic of Korea)

E-mail: wag@wag.caltech.edu, matlgen1@snu.ac.kr

Experimental details

We used Rhodizonic acid dihydrate (Alfa Aesar, 98%) and lithium carbonate (Sigma Aldrich, 99%) to synthesize $Li_4C_6O_6$. A small amount of de-ionized water (18 mL) was slowly added to the mixture consisting of rhodizonic acid dihydrate (1.828 g) and lithium carbonate (0.65 g). The solution was stirred over 10 hours at room temperature and then centrifuged at 4000 rpm for 15 minutes. The precipitate was rinsed with acetone. The final product, $Li_4C_6O_6$, was obtained by annealing the filtered powder at 673 K for 1 hour under an argon atmosphere.[1]

$Li_4C_6O_6$ was analyzed with an x-ray diffractometer (XRD, RIGAKU D/MAX-2500) using Cu Kα radiation (λ=1.518Å) with a scan range of 5-65° and a step size of 0.02° for 6 hours. Because the $Li_4C_6O_6$ is air sensitive, the XRD analysis was conducted under vacuum atmosphere.

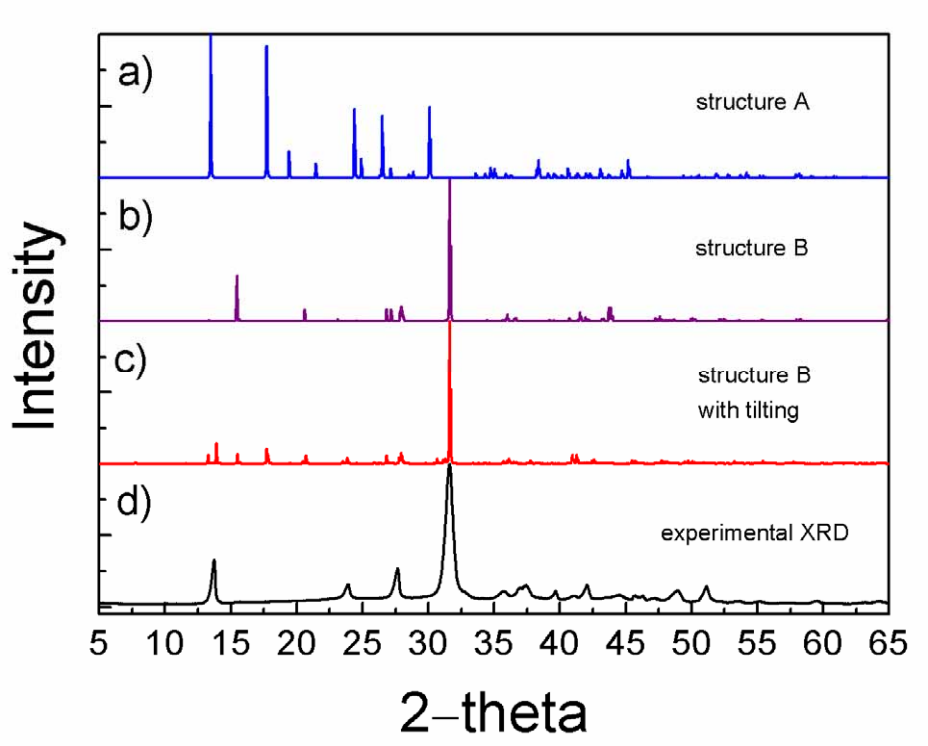

Figure S1. Comparison of XRD patterns from predicted $Li_4C_6O_6$ structures with experiment. The computed XRD patterns of (a) structures A, (b) structure B, and (c) structure B with tilting and (d) the experimental XRD of $Li_4C_6O_6$ obtained by annealing $Li_2C_6O_6$ under Ar at 673 K.[1]

Predicted structures by systematically generated a series of stacking patterns of the C_6O_6 layers

We systematically generated a series of stacking patterns of the C_6O_6 layers by gradually sliding the layers within the delithiated simulation cell of tilted structure B. We performed our multi-scale computational method with over 300 layered stacking C_6O_6 frameworks. Crystal structure parameters and DFT energies of 50 most stable structures are tabulated in Table S2. Atomic coordinates of the global minimum structure of $Li_4C_6O_6$, denoted as C, are tabulated in Table S3.

Table S2. Crystal structure parameters and DFT energies of top 50-ranked stable structures with various stacking patterns of the C_6O_6 layers within monoclinic simulation cell. The global minimum structure of $Li_4C_6O_6$ predicted with our multi-scale procedure is denoted as C.

Rank	space group	a	c	c	α	β	γ	Energy (eV / FU)
Structure C	C2/m	12.91	7.54	6.52	90.0	119.6	90.0	-112.838
2	P1	7.54	12.89	13.02	60.8	90.1	90.1	-112.762
3	Pm	12.78	13.01	7.55	90.0	90.0	61.2	-112.749
4	P1	7.53	7.57	11.70	99.6	71.6	119.5	-112.735
5	Pm	12.87	12.99	7.55	90.0	90.0	61.0	-112.728
6	P1	7.55	12.86	13.01	61.1	90.0	90.0	-112.720
7	P1	7.56	12.91	13.00	60.9	89.8	90.1	-112.709
8	P1	7.56	12.91	13.00	60.9	90.1	90.0	-112.706
9	$P2_1$	12.86	12.98	7.55	90.0	90.0	60.9	-112.704
10	P1	7.53	12.81	13.03	61.2	90.2	90.1	-112.701
11	P1	7.55	12.83	12.97	61.1	90.3	90.1	-112.695
12	P1	7.54	12.80	13.00	61.3	89.8	89.9	-112.694
13	P1	7.54	12.85	13.04	61.1	90.0	89.9	-112.688
14	P1	7.55	12.90	13.01	61.0	89.8	89.9	-112.681
15	P1	7.54	12.81	12.98	61.2	89.7	90.0	-112.678
16	Pm	13.00	13.13	7.53	90.0	90.0	59.5	-112.660
17	Pm	12.91	12.96	7.56	90.0	90.0	61.0	-112.658
18	Pc	12.79	13.00	7.52	90.0	90.0	61.5	-112.653
19	P1	7.52	12.81	13.00	61.3	90.0	89.9	-112.647
20	P1	7.56	12.35	13.14	64.0	89.9	89.8	-112.646
21	Cm	12.82	12.93	7.60	90.0	90.0	61.4	-112.644
22	P1	7.55	12.88	13.00	60.9	90.0	90.0	-112.638
23	P1	7.54	12.75	13.01	61.4	90.3	90.1	-112.634
24	P1	7.54	12.79	12.97	61.4	89.7	89.9	-112.630
25	P1	7.54	12.86	13.00	61.1	89.8	90.0	-112.630
26	P1	7.54	12.88	13.03	61.0	89.8	90.0	-112.621
27	Pm	12.98	13.13	7.56	90.0	90.0	59.5	-112.617
28	P1	7.55	12.95	13.02	60.7	90.1	90.1	-112.609
29	P1	7.57	12.89	12.92	61.5	90.2	90.0	-112.595
30	Pm	12.85	12.98	7.58	90.0	90.0	61.2	-112.588
31	Cm	12.99	13.11	7.51	90.0	90.0	60.4	-112.588
32	Pm	12.88	12.96	7.53	90.0	90.0	61.3	-112.588
33	P1	7.56	12.94	12.98	60.7	89.8	90.1	-112.585
34	P1	7.53	12.81	13.03	61.2	90.1	90.4	-112.581
35	P1	7.57	12.94	13.00	119.1	90.0	90.1	-112.579
36	P1	7.56	12.93	12.95	119.0	90.1	89.8	-112.575
37	Pm	12.98	13.04	7.54	90.0	90.0	60.6	-112.570

38	Cm	12.92	12.97	7.54	90.0	90.0	61.2	-112.561
39	P1	7.54	12.83	13.06	61.2	89.6	89.8	-112.557
40	Cm	12.83	13.06	7.52	90.0	90.0	60.7	-112.554
41	Cm	12.85	12.94	7.54	90.0	90.0	61.4	-112.548
42	P1	7.53	12.97	13.01	60.6	90.2	90.2	-112.543
43	P1	7.55	12.82	13.04	61.5	90.0	89.9	-112.541
44	Pm	12.81	13.02	7.54	90.0	90.0	61.1	-112.531
45	Cm	12.84	13.00	7.61	90.0	90.0	61.0	-112.526
46	P1	7.59	12.85	12.93	61.5	89.8	90.0	-112.525
47	P1	7.58	12.87	12.91	118.6	90.0	89.9	-112.518
48	P1	7.55	12.86	12.88	118.4	89.9	90.2	-112.514
49	Pm	12.89	13.02	7.55	90.0	90.0	61.0	-112.512
50	Pm	12.88	13.07	7.56	90.0	90.0	60.8	-112.508
Structure A	$P2_1/c$	5.11	5.36	13.58	90.0	105.1	90.0	-111.699
Structure B	Cm	13.23	11.39	7.67	90.0	90.0	90.0	-111.704

Table S3. Lattice parameters and atomic coordinates for the global minimum structure of $Li_4C_6O_6$ predicted with our multi-scale procedure (structure C). The Space group is C2/m (No. 12) with cell parameters of a=12.917, b=7.541, c=6.523, α=90°, β=119.6°, and γ=90°

Atom	Site	*x*	*y*	*z*	Occupancy
Li1	8j	0.82427	0.24213	0.35720	1
Li1'	4i	0.58922	0	0.83938	1
Li2	4i	0.64780	0	0.30710	1
C1	8j	0.00466	0.16488	0.78023	1
C2	8j	0.11548	0.16490	0.99828	1
C3	4i	0.94841	0	0.67227	1
C4	4i	0.17288	0	0.10187	1
O1	8j	0.95928	0.31491	0.67396	1
O2	8j	0.16748	0.68511	0.09248	1
O3	4i	0.85091	0	0.46874	1
O4	4i	0.28001	0	0.28618	1

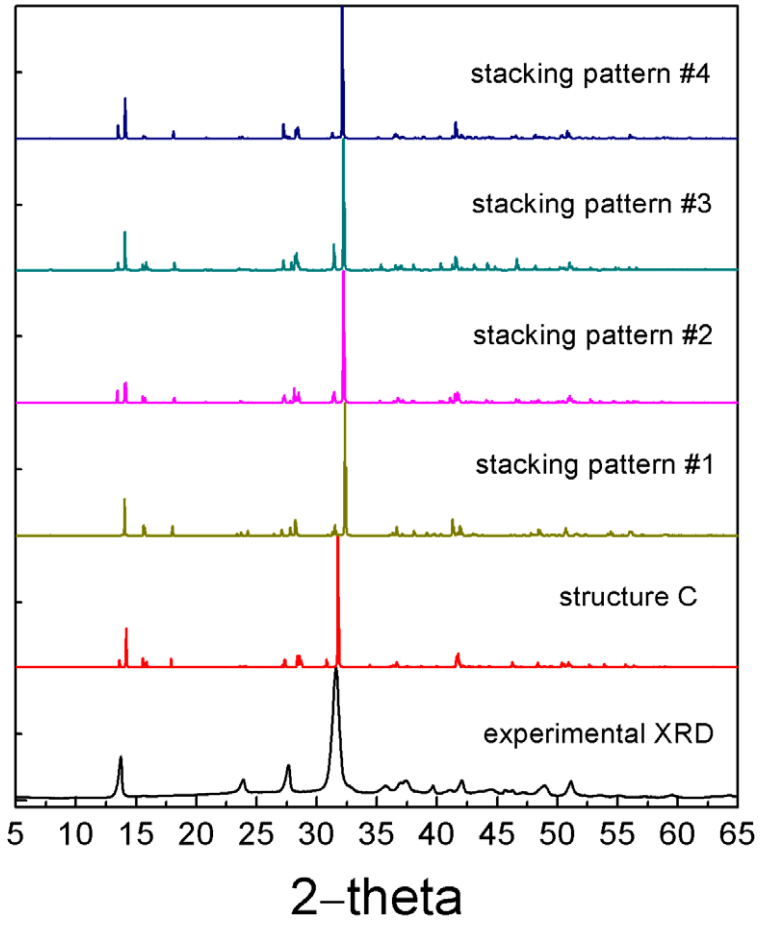

Figure S4. Comparison of XRD patterns from predicted stable $Li_4C_6O_6$ structures with experiment. The intensities of major peaks slightly alter with the stacking pattern of the C_6O_6 layers.

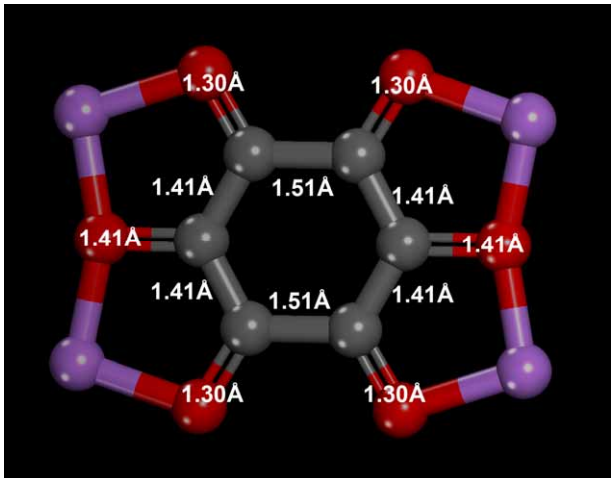

Figure S5. The C-C and C-O bond lengths of $Li_4C_6O_6$ molecule calculated with GAUSSIAN 03 program using B3LYP hybrid exchange-correlation functional. (Violet: Li, Grey: C, Red: O)

Predicted structures by random stacking of C_6O_6

We considered various C_6O_6 frameworks with possible packing arrangements in all 14 reasonable space groups. We used the *Polymorph* in MS modeling version 4.2 (Accelrys Inc.)[2] to generate possible C_6O_6 stackings for the 14 most plausible space groups.[3] This module efficiently examines the large search domain by using Monte Carlo simulated annealing process (MC-SA), and generates thousands of possible C_6O_6 packing arrangements. We generated 113 possible C_6O_6 frameworks, as tabulated in Table S6, and performed our multi-scale computational method with these frameworks and obtain crystal structures the lowest 20 of which are in Table S7.

Table S6. Proposed crystal structures of $Li_4C_6O_6$ with various space groups.

space group	no.	# of proposed structure	f.u. in unit cell
P-1	2	1	8 $Li_4C_6O_6$
$P2_1$	4	10	4 $Li_4C_6O_6$
C2	5	13	4 $Li_4C_6O_6$
Cc	9	2	4 $Li_4C_6O_6$
P2/m	10	3	4 $Li_4C_6O_6$
$P2_1/m$	11	1	4 $Li_4C_6O_6$
C2/m	12	4	8 $Li_4C_6O_6$
P2/c	13	16	4 $Li_4C_6O_6$
$P2_1/c$	14	29	4 $Li_4C_6O_6$
C2/c	15	2	8 $Li_4C_6O_6$
$P2_12_12_1$	18	12	4 $Li_4C_6O_6$
$Pna2_1$	33	2	4 $Li_4C_6O_6$
Pbcn	60	17	8 $Li_4C_6O_6$
Pbca	61	1	8 $Li_4C_6O_6$

Table S7. The crystal structure parameters and DFT energy of twenty-ranked stable structures among 113 random stacking $Li_4C_6O_6$ structure. Structures are denoted by DFT energy ranking among 113 random stacking $Li_4C_6O_6$ structure and initial space group for random stacking C_6O_6 frameworks. Final space groups are for predicted $Li_4C_6O_6$ structures.

Structure	final space group	*a*	*b*	*c*	α	β	γ	Energy (eV / FU)
Structure C	C2/m	12.91	7.54	6.52	90.0	119.6	90.0	-112.838
1- C2/c	P2/m	7.04	7.70	20.84	90	97.7	90	-112.731
2- C2	C2/m	7.05	7.70	11.75	90	118.5	90	-112.695
3- P2/c	Pm	10.41	7.71	7.05	90	98	90	-112.681
4-P2/c	Pm	13.47	7.7	5.75	90	100.5	90	-112.454
5-$P2_1/c$	$P2_1$	7.05	6.68	7.77	90	60.7	90	-112.442
6-$P2_1/c$	P1	10.15	8.63	7.57	91.1	70.6	89.5	-112.439
7-Pbcn	P1	11.29	7.66	13.7	90	90	90	-112.429
8-$P2_1/c$	$Cmc2_1$	8.01	6.64	22.08	90	90	90	-112.420
9-Pbca	$P2_12_12_1$	15.1	13.18	5.63	90	90	90	-112.417
10-Pbcn	P1	5.58	15.39	13.33	90	90	90	-112.401
11-$P2_1$	R3m	7.81	7.81	8.39	90	90	120	-112.395
12-$P2_1$	$P2_1$	10.19	11.81	5.1	90	104.1	90	-112.345
13-$Pna2_1$	Pnma	5.66	7.75	13.42	90	90	90	-112.343
14-$P2_1/c$	$Pmn2_1$	7.98	6.33	11.88	90	90	90	-112.321
15-$P2_12_12_1$	Pnma	6.69	7.81	11.08	90	90	90	-112.299
16-$P2_1/c$	P1	5.68	7.74	13.4	90	90	98.6	-112.298
17-P2/c	$P2_1/c$	11.78	6.33	14.16	90	146	90	-112.293
18-$P2_1/c$	Pnma	5.79	7.76	13.1	90	90	90	-112.287
19-P2/c	P1	7.13	7.79	10.53	90	82.7	90	-112.276
20-$P2_1/c$	Cm	13.43	7.76	5.7	90	81.3	90	-112.267

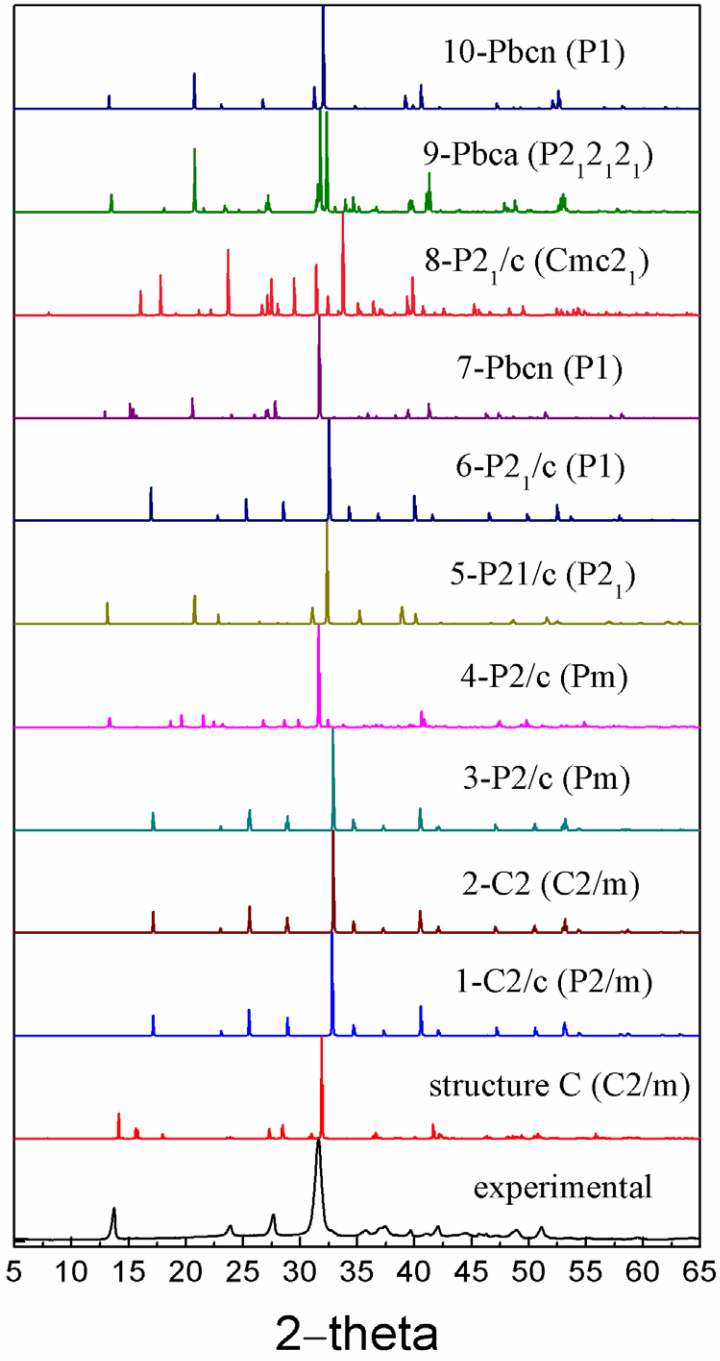

Figure S8. Comparison of XRD patterns from stable predicted $Li_4C_6O_6$ structures among random stacking structure in Table S7 with experiment.

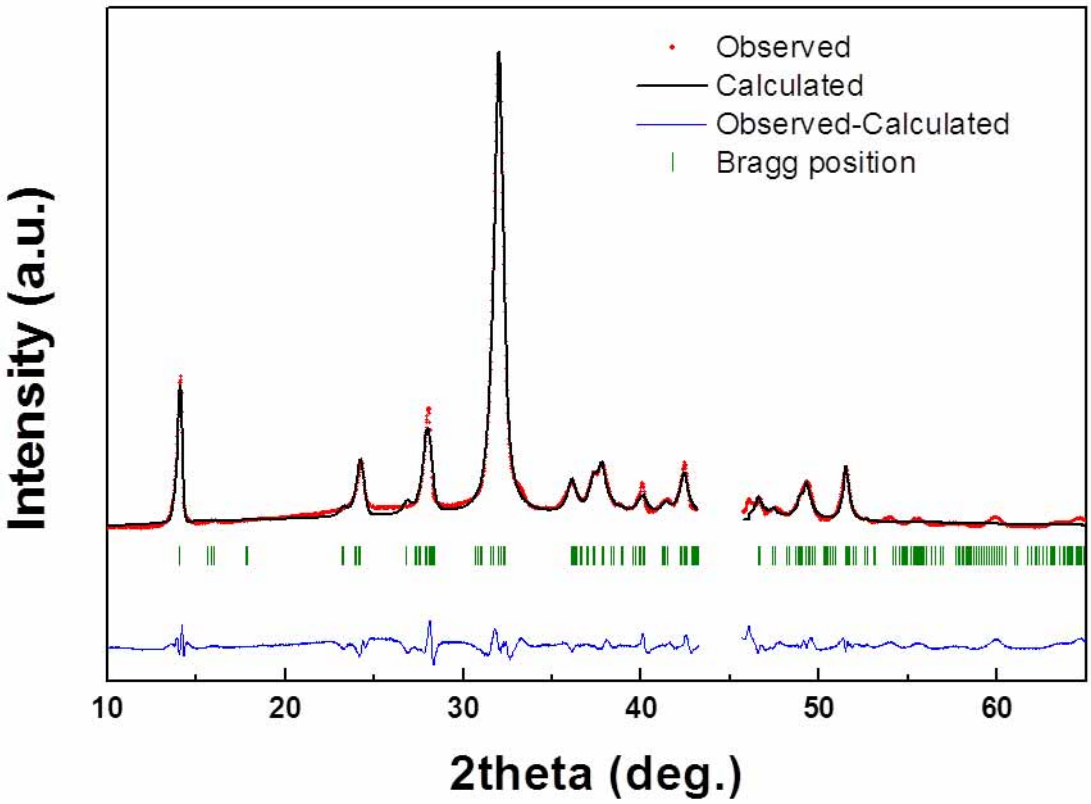

Figure S9. X-ray diffraction pattern (Red dotted line) compared to the profile matching pattern with structure C (black solid line) and difference between experimental and calculated pattern. (blue solid line)

Profile matching of the XRD patterns with the structure C was performed using Fullprof software[4] and resulted in lattice parameters of a= 12.78 (1) b=7.663 (8) c=6.5278 (7) β = 119.832 (4). R-Factors were R_p=7.45, R_I=0.876, R_F=0.710 and chi^2=0.0882.

References

(1) Chen, H.; Armand, M.; Courty, M.; Jiang, M.; Grey, C. P.; Dolhem, F.; Tarascon, J.-M.; Poizot, P. *J. Am. Chem. Soc.* **2009**, *131*, 8984.

(2) Accelrys, *Material Studio Release Notes, Release 4.2, Accelrys Software, San Diego* (**2006**).

(3) Baur, W. H.; Kassner, D. *Acta Crystallogr., Sect. B*, **1992**, 48, 356.

(4) Rodríguez Carvajal, *Physica B,* **1993**, 192, 55