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Magnesium-based systems for carbon dioxide capture, storage and recycling: from leaves to synthetic nanostructured materials

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S1. Calculations for Figure 2.

In order to allow a more effective visualization of the enormous amount of CO_2 excess in the atmosphere, Figure 2 in the Manuscript has been created by a quantitative estimation of the volumes occupied by storing it as liquid CO_2 or by converting in magnesium carbonate. These volumes have been expressed by using a famous skyscraper and a well-known mountain as volume unit, respectively. A similar calculation has been carried out by considering the fixation of CO_2 in dry wood in a fast growing plant (hybrid poplar).

Excess CO_2 in the atmosphere: $9 \cdot 10^{11}$ tons (Ref. 1)

Liquid density (at -20 °C (or -4 °F) and 19.7 bar): 1256.74 $kg \cdot m^{-3}$ (http://encyclopedia.airliquide.com/)

Solid density: 1562 $kg \cdot m^{-3}$ (http://encyclopedia.airliquide.com/)

that corresponds to:

1) $7.16 \cdot 10^{11}$ m^3 liquid CO_2;

2) $5.76 \cdot 10^{11}$ m^3 solid CO_2;

3) 254 946 containers of liquid CO_2 having the Empire state building shape;

calculated by using the Empire state building dimensions (as measured by using the data in Google Maps: https://www.google.it/maps/):

68.9 x 92.0496 x 443 m (h) = 2.81E+06 m^3

4) 18.17 mountains of $MgCO_3 \cdot 5\ H_2O$ having the same height of Monviso;

calculated by approximating a mountain to a square pyramid with an angle at the basis of 30° and height 3842 m (http://it.wikipedia.org/), resulting in a volume for each mountain of $1.13 \cdot 10^{11}$ m^3.

Density of $MgCO_3 \cdot 5\ H_2O$: 1.73 $g \cdot cm^{-3}$ (http://it.wikipedia.org/).

If it is considered 1 CO_2 molecule fixed per formula unit, $3.57 \cdot 10^{15}$ kg of $MgCO_3 \cdot 5\ H_2O$ would be necessary, that corresponds to a volume of $2.06 \cdot 10^{12}$ m^3.

5) 2 year-old wood of hybrid poplars covering an area equal to the total Earth surface;

considering that this plant can provide:

$3.09 \cdot 10^2$ - $1.98 \cdot 10^3$ tons/km^2/year of dry wood

(http://www.extension.org/pages/70456/poplar-populus-spp-trees-for-biofuel-production#.VGfRr_mG98F)

and considering that 1 kg of CO_2 is fixed in 2 kg of dry wood[2]

in the most optimistic hypothesis a wood covering a surface of $5.10 \cdot 10^8$ km^2 would fix the CO_2 excess in the atmosphere in 1.79 years.

This wood, considering the average weigh density of dry wood of hybrid poplar species[3] of 0.45 $g \cdot cm^{-3}$, would occupies $3.96 \cdot 10^{12}$ m^3 that is only 5.52 times the volume that would be occupied by storing the same amount as liquid CO_2.

S2. Calculations for Table 8.

The calculations made to obtain an estimate of the time needed to capture the CO_2 excess from the atmosphere in the three speculative systems reported in Table 8 are here explicitated.

i) In the case of separation by using MOFs as scrubbers, the first step is to fix the amount of MOFs that will be used. In the other two cases (mine tailings and hybrid poplar forest), this amount is implicit when it is fixed the surface occupied. In this case, on the contrary, the MOF quantity to be used was normalized to the surface occupied by the other two systems (Earth land surface) by considering to coat it with a layer 1 cm in thickness.

The XRD density of IRMOF-74-II-mmem as in the structure reported in Ref. 4 is 1073.2 kg m^{-3}.

The surface occupied by the land is 148940000 km^2, that is the total volume of MOF is 1489,4 km^3 that is $1.4894 \cdot 10^{12}$ m^3. Its mass is then $1.59 \cdot 10^{15}$ kg.

For this MOF, the CO_2 adsorbed at 0.3 mbar and RT is 1.8 mol g^{-1} that is 0.0792 tons of CO_2 per ton of MOF. Supposing that the adsorption in each CC cycle is completed in 15 min and the regeneration of the sample is obtained in the same time (15 min), this means that in 1 year, 17520 ads/des cycles can be completed. 1 ton of MOF would be able to capture in 1 year:

$1387.584 \cdot 17520 = 1387.584$ ton CO_2 ton^{-1} MOF

In order to capture 900 Gtons in 1 year:

$900 \cdot 10^9 / 1387.584 = 6.486\ 10^{11}$ tons of MOF would be necessary.

If the amount of $1.59 \cdot 10^{15}$ kg is used:

$6.486\ 10^{11}/1.59 \cdot 10^{12} = 0.406$ year

will be sufficient.

ii) Mineralization. In this case, the rates of mineralization adopted were the ones reported for carbon fixation due to natural weathering in Ref. for mafic/ultramafic mine tailing that is 27 and 1330 gC m^{-2} $year^{-1}$, that correspond to 99 and 4876.7 gCO_2 m^{-2} $year^{-1}$.[5] Considering a surface equal to the Earth's land surface this means that, in order to fix all the CO_2 excess, 61.04 and 1.24 year would be necessary.

iii) Photosynthesis. An hybrid poplar forest was considered, having a grow rate in the range 309 and 1980 tons wood km^{-2} $year^{-1}$. This correspond to about 154.5 and 990 tons CO_2 km^{-2} $year^{-1}$. This means that, having care of this forest, the 900 Gtons of CO_2 would be fixed in 6.11 or 39.1 years.

S3. Review of Mg-based metal organic framework.

A comprehensive review of Mg-based MOFs is reported in Table S1.

Table S1. *Review of Mg-based MOFs reported in literature reporting the magnesium Coordination Number (CN), framework dimensionality, BET (S_{BET}) and Langmuir ($S_{Langmuir}$) surface area and pore volume(V_{por}).*

Material[a]	CN[b]	Framework dimensionality	S_{BET}[c] ($m^2\ g^{-1}$)	$S_{Langmuir}$[c] ($m^2\ g^{-1}$)	V_{por}[c] ($cm^3\ g^{-1}$)	Ref.
$[Mg_3(ndc)_3(def)_4]$	6 (2 DEF)	3D	low (accessible to H_2 and O_2)	low (accessible to H_2 and O_2)	–	6, 7
[Mg(DMF)(μ-BDC)]	6 (1 DMF)	3D	–	–	–	8
$(Mg_{12}(H_2O)_{12}(\mu_2\text{-}(H_2O)_6)(btb)_8(dioxane)_6)\cdot\sim$11 dioxane (MIL-123)	6 (3 H_2O)	3D	216	–	–	9, 10
$\{[Mg(Hidc)(H_2O)_2]\cdot 1.5\ H_2O\}_n$	6 (2 H_2O)	1D	low	low	0.06	11
$[Mg\text{-}(Hidc)(H_2O)]_n$	6 (1 H_2O)	2D	–	–	–	11
$\{[Mg_3(idc)_2(H_2O)_5]\cdot 2\ H_2O\}_n$	6 (3 H_2O)	3D	low	low	0.02	11
MgTTTP (PCN-72)	6 (1 DMSO)	3D	low	low	low	12
$[Mg_2(HCO_2)_2(NH_2\text{-BDC})\text{-}(DMF)_2]_n$	6 (1 DMF)	2D	–	–	–	13
$[Mg_2(HCO_2)_2(NH_2\text{-BDC})\text{-}(DMF)_2]_n$	6 (1 DMF)	3D	–	–	–	13
$\alpha\text{-}[Mg_3(O_2CH)_6\cdot 2\ H_2O]$	6 (4 H_2O)	3D	–	–	–	10
$\beta\text{-}[Mg(HCOO)_2\cdot 2\ H_2O]$	6 (2 H_2O)	3D	–	–	–	14
$\{H[Mg(HCOO)_3]\supset NHMe_2\}$	6 (0)	3D	–	–	–	15
$\alpha\text{-}[Mg_3(O_2CH)_6]$	6 (0)	3D	150	–	0.11	16
$\beta\text{-}[Mg_3(O_2CH)_6]$	6 (0)	3D	–	–	–	10
$\gamma\text{-}[Mg_3(O_2CH)_6]$	6 (0)	3D	120	–	24.7 vol.%[d]	17
$Mg(HCOO)_2(HCOOH)\supset(CH_3)_2NH$ ($R\underline{3}c$)	6 (0)	3D	–	–	–	14
$[HONH_3][Mg(HCOO)_3]$	6 (0)	–	–	–	–	18
$[(Fmd)Mg(HCOO)_3]$	6 (0)	3D	low	low	low	19
$[(Gua)Mg(HCOO)_3]$	6 (0)	3D	low	low	low	19
$\{[Mg_2(H\text{-}3,5\text{-}PZDC)_2(H_2O)_4]\cdot H_2O\}_n$	6 (2 H_2O)	2D	low	low	low	20
$Mg_3(bdc)_3(DMA)_4$	6 (2 DMF)	2D	–	–	–	21
$Mg_3(bdc)_3(EtOH)_2$	6 (1 EtOH)	3D	–	–	33.1 vol.%[d]	21
$Mg_3(bpdc)_3(DMA)_4$	6 (2 DMA)	3D	–	–	45.5 vol.%[d]	21
$Mg(H_{1.5}btc)_2/_3(btc)_1/_3(DMA)_2\cdot(DMA)_1/_3$	6 (2 DMA)	2D	–	–	15.4 vol.%[d]	21
$[Mg(3,5\text{-}PDC)(H_2O)]$ (Mg-MOF-1)	6 (1 H_2O)	3D	–	–	38.7 vol.%	22
$[Mg(2,4\text{-}PDC)(H_2O)_3]$ (MgMOF-2)	6 (3 H_2O)	0D	–	–	–	22
$[Mg_2(NDA)_2(H_2O)_3]\cdot 0.25\ H_2O$	6 (2 H_2O)	3D	–	–	–	23
$[Mg(H_2O)_4(phen)_2]$ hfpb (α-AEPF-14)	6 (4 H_2O)	0D	–	–	–	24
$[Mg(H_2O)_4(phen)_2]$ hfpb (β-AEPF-14)	6 (4 H_2O)	0D	–	–	–	24
$[Mg(Hhfpb)_2(phen)]$ AEPF-15	6 (0)	1D	–	–	–	24
$Mg(H_2O)_2(hfpb)(phen)$ (AEPF-16)	6(2 H_2O)	1D	–	–	–	24
$Mg(H_2O)(hfpb)(phen)$ (AEPF-17)	6 (1 H_2O)	2D	–	–	–	24
$[Mg(dmf)_2(H_2O)_4]$ndc	6 (4 H_2O)	0D	–	–	–	6
$Mg_3(ndc)_3(dif)_4Mg_3(ndc)_3(dif)_4$	6 (0)	2D	low	low	low	25
$[Mg_3(ndc)_3(dmf)_4]$ (TUDMOF-2)	6 (0)	3D	–	520	0.17	6
$[Mg_3(ndc)_3(dmf)_2(CH_3OH)\text{-}(H_2O)](dmf)$ (TUDMOF-3)	6 (1 DMF + 1 H_2O/MeOH)	3D	418	632	0.21	25
$Mg(H_2dobdc)$ (CPO-26-Mg)	6 (2 H_2O)	3D	–	–	–	26
$Mg_2(dobdc)$ (CPO-27-Mg, Mg/DOBDC, MOF-74-Mg, IRMOF-74-I)[e]	6 (1 H_2O)	3D	877[26] 1495[27] 1350[28] 1542[29] 1800[30] 780[31]	1030[26] 1905[27] 1600[28] 2060[30] 886[31]	0.37[26] 0.60[28] 0.21[31]	26-29, 32
$Mg_2(dobpdc)$, IRMOF-74-IIb	6 (1 H_2O)	3D	2510[e,28]	2940[e,28]	1.04[e,28] 1.16[4]	28
IRMOF-74-III[e]	6 (1 H_2O)	3D	2440	3750	1.23	28
IRMOF-74-IV[e]	6 (1 H_2O)	3D	2480	5370	1.60	28
IRMOF-74-V[e]	6 (1 H_2O)	3D	2230	6940	1.89	28
IRMOF-74-V-hex[e]	6 (1 H_2O)	3D	1680	4450	1.29	28
IRMOF-74-VI[e]	6 (1 H_2O)	3D	1600	5880	1.65	28
IRMOF-74-VII[e]	6 (1 H_2O)	3D	1800	8320	2.12	28
IRMOF-74-VII-oeg[e]	6 (1 H_2O)	3D	2230	3321	0.89	28
IRMOF-74-IX[e]	6 (1 H_2O)	3D	1920	9410	2.51	28
IRMOF-74-XI[e]	6 (1 H_2O)	3D	1760	9880	3.41	28
IRMOF-74-III-CH_3	6 (1 H_2O)	3D	2640	3940	1.37	33
IRMOF-74-III-NH_2	6 (1 H_2O)	3D	2720	4130	1.44	33
IRMOF-74-III-CH_2NHBoc	6 (1 H_2O)	3D	2170	2720	0.95	33

IRMOF-74-III-CH_2NH_2	6 (1 H_2O)	3D	2310	3270	1.14	33
IRMOF-74-III-CH_2NMeBoc	6 (1 H_2O)	3D	2220	2540	0.89	33
IRMOF-74-III-CH_2NHMe	6 (1 H_2O)	3D	2250	3150	1.13	33
IRMOF-74-I-ED	6 (1 ED)	3D	–	469	0.40	34
IRMOF-74-I-TEPA-30	6 (1 TEPA)	3D	312.63	410.68	0.19	31
IRMOF-74-I-TEPA-40	6 (1 TEPA)	3D	132.24	230.5	0.15	31
IRMOF-74-I-TEPA-50	6 (1 TEPA)	3D	23.54	54.21	0.05	31
$Mg(dobpdc)_2$-mmen	6 (1 mmen)	3D	–	–	0.02	4
$[Mg(H_2O)_6](L)_2\cdot 2H_2O$	6 (6 H_2O)	3D	–	–	–	35
$[Mg_3(HCOO)_4$(D-Cam)$]_n$	6 (0)	3D	–	–	–	36
$Mg(OBA)(H_2O)_2$	6 (2 H_2O)	2D	–	–	–	37
$Mg_2(BTC)(CH_3COO)(DMA)_3\cdot H_2O$	6 (3 DMA)	3D	low	low	low	38
Mgtarts	6 (0-2 H_2O)	0D-3D	low	low	low	39
$Mg(C_10H_{19}O_2)_2(H_2O)_3$	6 (3 H_2O)	2D	–	–	–	40
$Mg(C_7H_{13}O_2)_2(H_2O)_3$	6 (3 H_2O)	2D	–	–	–	40
$Mg(H_2O)_2(C_4O_4)$	6 (2 H_2O)	3D	low	low	low	41
$Mg(H_2O)(C_4H_4O_5)\cdot H_2O$	6 (1 H_2O)	3D	low	low	low	41
$Mg(C_5H_6O_4)$	6 (2 H_2O)	2D	low	low	low	41
$K_2Mg(H_2O)_2(C_8H_4O_8)$	6 (2 H_2O)	3D	low	low	low	41
$Mg(BDC)(H_2O)_2$	6 (2 H_2O)	3D	–	–	–	42
$\{[Mg(BPTC)0.5\text{-}(H_2O)_3]\cdot 5H_2O\}_n$	6 (2 H_2O)	2D	–	–	–	43
$[Mg(DMF)(\mu\text{-}BDC)]_\infty$	6 (1 DMF)	3D	–	–	–	8
$[Mg_3(DMF)_4(\mu\text{-}NDC)_3]_\infty$	6 (2 DMF)	3D	–	–	–	8
$[Mg_3(DEF)_4(\mu\text{-}NDC)_3]_\infty$	6 (2 DEF)	3D	–	–	–	8
[MgBTC(OCN)$_2\cdot 2H_2O$] (MgBTC)	6 (2 OCN)	2D	–	–	–	44
[(Mg_3(bpdc)$_3$4DMF) ⊃ 3.8 DMF]	6 (1 DMF)	3 D	–	–	–	45
$Mg_3(BDC)_3(DMSO)_4$	6 (2 DMSO)	3D	–	–	–	45
[Mg(TCPBDA)$(H_2O)_2$] ·6DMF ·6H_2O (SNU-25)	6 (2 H_2O)	3D	low	low	low	46

[a] NH_2-BDC = 2-amino-1,4-benzenedicarboxylate; DMF = *N*,*N*-dimethylformamide, H_2bdc = 1,4-benzenedicarboxylic acid, DMA = dimethylacetamide, H_2bpdc = 4,4-biphenyldicarboxylic acid, H_3btc = 1,3,5-tricarboxylic acid, H_2-3,5-PDC = 3,5-pyridine dicarboxylic acid, H_2-2,4-PDC = 2,4-pyridine dicarboxylic acid, H_3-3,5-PZDC = pyrazole-pyridine dicarboxylic acid; H_2NDA = 1,4-naphthalenedicarboxylic acid, phen = 1,10-phenantroline, H_2hfpb = (hexafluoroisopropylidene)bis(benzoic acid); def = N,N-diethylformamide; ndc = 2,6-naphthalenedicarboxylate; D-H_2Cam = D-camphoric acid; DMA = dimethylacetamide; H_2tart = tartaric acid, dif = N,N-diisopropylformamide; H_2OBA = 4,49-oxybisbenzoic acid; H_4dobdc= 2,5-dihydroxy-1,4-benzene-dicarboxylic acid; BPTC = 2,2',6,6'-tetracarboxybiphenyl; Boc =tertbutyloxycarbonyl; H_3idc = 4,5-imidazoledicarboxylic acid; H_4TTTP = 2′,3′,5′,6′-tetramethyl-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid; formamidinium cation [Fmd^+, (NH_2–CH^+–NH_2)]; guanidinium cations[Gua^+,$C^+(NH_2)_3$]; TCPBDA^{2-} = N,N,N',N'-tetrakis(4-carboxyphenyl)-biphenyl-4,4'-diamine, ED = etilendiamine; TEPA = tetraethylenepentamine; mmen = N,N'-dimethylethylenediamine; BTC = 1,3,5-benzenetricarboxylate.

[b] In parenthesis the number and the nature of solvent molecules coordinated to the most exposed Mg^{2+} species is reported.

[c] Surface area and pore volume as obtained from N_2 adsorption, if not otherwise specified.

[d] Calculated value upon manual removal of the solvent molecules from the solvated structure.

[e] Ar isotherm and variable BET range.

References

1. M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43-81.
2. S. H. Lamlom and R. A. Savidge, *Biomass Bioen.*, 2003, **25**, 381-388.
3. A. Pliura, S. Y. Zhang, J. MacKay and J. Bousquet, 2007, **238**, 92-106.
4. T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 7056-7065.
5. H. C. Oskierski, B. Z. Dlugogorski and G. Jacobsen, *Chem. Geol.*, 2013, **358**, 156-169.
6. I. Senkovska and S. Kaskel, *Eur. J. Inorg. Chem.*, 2006, **2006**, 4564-4569.
7. M. Dinča and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376-9377.
8. C. A. Williams, A. J. Blake, C. Wilson, P. Hubberstey and M. Schröder, *Cryst. Growth Des.*, 2008, **8**, 911-922.
9. C. Volkringer, T. Loiseau, J. Marrot and G. Ferey, *Cryst. Eng. Comm.*, 2009, **11**, 58-60.

10. D. Banerjee and J. B. Parise, *Cryst. Growth Des.*, 2011, **11**, 4704-4720 and references therein.
11. K. L. Gurunatha, K. Uemura and T. K. Maji, *Inorg. Chem.*, 2008, **47**, 6578-6580.
12. Y. Liu, Y.-P. Chen, T.-F. Liu, A. A. Yakovenko, A. M. Raiff and H.-C. Zhou, *Cryst. Eng. Comm.*, 2013, **15**, 9688-9693.
13. L. Han, L. Qin, X. Z. Yan, L. P. Xu, J. L. Sun, L. Yu, H. B. Chen and X. D. Zou, *Cryst. Growth Des.*, 2013, **13**, 1807-1811.
14. A. Rossin, A. Ienco, F. Costantino, T. Montini, B. Di Credico, M. Caporali, L. Gonsalvi, P. Fornasiero and M. Peruzzini, *Cryst. Growth Des.*, 2008, **8**, 3302-3308.
15. A. Rossin, D. Fairen-Jimenez, T. Dueren, G. Giambastiani, M. Peruzzini and J. G. Vitillo, *Langmuir*, 2011, **27**, 10124-10131.
16. J. A. Rood, B. C. Noll and K. W. Henderson, *Inorg. Chem.*, 2006, **45**, 5521-5528.
17. A. Mallick, S. Saha, P. Pachfule, S. Roy and R. Banerjee, *Inorg. Chem.*, 2011, **50**, 1392-1401.
18. B. Liu, R. Shang, K. L. Hu, Z. M. Wang and S. Gao, *Inorg. Chem.*, 2012, **51**, 13363-13372.
19. A. Rossin, M. R. Chierotti, G. Giambastiani, R. Gobetto and M. Peruzzini, *Cryst. Eng. Comm.*, 2012, **14**, 4454-4460.
20. D. Saha, T. Maity, S. Das and S. Koner, *Dalton Trans.*, 2013, **42**, 13912-13922.
21. R. P. Davies, R. J. Less, P. D. Lickiss and A. J. P. White, *Dalton Trans.*, 2007, 2528-2535.
22. A. Mallick, S. Saha, P. Pachfule, S. Roy and R. Banerjee, *J. Mater. Chem.*, 2010, **20**, 9073-9080.
23. D. S. Raja, J. H. Luo, C. T. Yeh, Y. C. Jiang, K. F. Hsu and C. H. Lin, *Cryst. Eng. Comm*, 2014, **16**, 1985-1994.
24. A. E. Platero-Prats, V. A. de la Pena-O'Shea, D. M. Proserpio, N. Snejko, E. Gutierrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 2012, **134**, 4762-4771.
25. I. Senkovska, J. Fritsch and S. Kaskel, *Eur. J. Inorg. Chem.*, 2007, **2007**, 5475-5479.
26. P. D. C. Dietzel, R. Blom and H. Fjellvåg, *Eur. J. Inorg. Chem.*, 2008, **2008**, 3624-3632.
27. S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870-10871.
28. H. X. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018-1023.
29. P. D. C. Dietzel, V. Besikiotis and R. Blom, *J. Mater. Chem.*, 2009, **19**, 7362-7370.
30. Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 5664-5667.
31. Y. Cao, F. Song, Y. Zhao and Q. Zhong, *J. Environ. Sci.*, 2013, **25**, 2081-2087.
32. L. Valenzano, B. Civalleri, S. Chavan, G. Turnes Palomino, C. Otero Areán and S. Bordiga, *J. Phys. Chem. C*, 2010, **114**, 11185-11191.
33. A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 8863-8866.
34. S. Choi, T. Watanabe, T.-H. Bae, D. S. Sholl and C. W. Jones, *J. Phys. Chem. Lett.*, 2012, **3**, 1136-1141.
35. Y. Q. Huang, H. D. Cheng, B. L. Guo, Y. Wan, H. Y. Chen, Y. K. Li and Y. Zhao, *Inorg. Chim. Acta*, 2014, **421**, 318-325.
36. J. Zhang, S. Chen, H. Valle, M. Wong, C. Austria, M. Cruz and X. Bu, *J. Am. Chem. Soc.*, 2007, **129**, 14168-14169.

37. P. C. Cheng, F. S. Tseng, C. T. Yeh, T. G. Chang, C. C. Kao, C. H. Lin, W. R. Liu, J. S. Chen and V. Zima, *Cryst. Eng. Comm.*, 2012, **14**, 6812-6822.
38. S. Ma, J. A. Fillinger, M. W. Ambrogio, J.-L. Zuo and H.-C. Zhou, *Inorg. Chem. Commun.*, 2007, **10**, 220-222.
39. K. C. Kam, K. L. M. Young and A. K. Cheetham, *Crys. Growth Des.*, 2007, **7**, 1522-1532.
40. A. Mesbah, C. Juers, F. Lacouture, S. p. Mathieu, E. Rocca, M. François and J. Steinmetz, *Solid State Sci.*, 2007, **9**, 322-328.
41. Z. Hulvey and A. K. Cheetham, *Solid State Sci.*, 2007, **9**, 137-143.
42. J. A. Kaduk, *Acta Cryst. Sec. B*, 2002, **58**, 815-822.
43. X.-Y. Dong, X.-P. Hu, H.-C. Yao, S.-Q. Zang, H.-W. Hou and T. C. W. Mak, *Inorg. Chem.*, 2014, **53**, 12050-12057.
44. L.-F. Song, C.-H. Jiang, J. Zhang, L.-X. Sun, F. Xu, Y.-Q. Tian, W.-S. You, Z. Cao, L. Zhang and D.-W. Yang, 2010, **101**, 365-370.
45. J. A. Rood, B. C. Noll and K. W. Henderson, *Main Group Chem.*, 2006, **5**, 21-30.
46. Y. E. Cheon, J. Park and M. P. Suh, *Chem. Commun.*, 2009, 5436-5438.