# **Electronic Structure of 1,3-dicarbomethoxy4,6benzenedicarboxylic acid: Density Functional Approach**

Sikander Azam<sup>1,\*</sup>, A. H. Reshak<sup>1,2</sup>

 <sup>1</sup> Institute of complex systems, FFPW, CENAKVA-South Bohemia University CB, Nove Hrady 37333, Czech Republic
<sup>2</sup>Center of Excellence Geopolymer and Green Technology, School of Material Engineering, University Malaysia Perlis, 01007 Kangar, Perlis, Malaysia
\*E-mail: <u>sikander.physicst@gmail.com</u>

Received: 27 May 2013 / Accepted: 29 June 2013 / Published: 1 August 2013

Structural optimization of 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid single crystal was performed by minimizing the forces which act on the atoms. The optimized geometry was used to perform the theoretical study of electronic properties, electronic charge density and optical properties. Electronic structure, electronic charge density and optical properties were investigated using the full potential linear augmented plane wave based on the first-principles density functional theory (DFT). The exchange correlation (XC) effects are taken in to account by Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) and modified Becke Johnson (MBJ) potential. The band structure shows that the calculated compound has an indirect band gap of 2.99, 3.05 and 3.93 eV for LDA, GGA and mBJ respectively. The electron charge densities were also analyzed and discussed. The charge densities indicate that bonding between H-O, C-C and O-O is mainly covalent and the bonding between O is mainly ionic. The complex dielectric function, refractive index, energy-loss spectrum and reflectivity have been calculated.

Keywords: electronic structure, electronic charge density and optical properties: DFT

# **1. INTRODUCTION**

In various fields a variety of application has been found of Schiff base ligands and their metal which includes magnetism, medical imaging, industrial use as a catalyst and biology etc [1-10]. The most important one for building block to prepare open frame work material is Poly-carboxylic acids of benzene [11–17]. In which benzene tricarboxylic acid has adaptability [11] and can figure a variety of motifs both through metal co-ordination [11,12, 18–21] or by way of organic motifs which posses

complimenting hydrogen bonding effect [11, 22–24]. The, carboxylic acid have numerous binding sites and possibly will have analogous co-ordination chemistry to phthalimide derivative like (1,3-dioxo-1,3dihydro-isoindol-2-yl)-acetic acid [25, 26]. The 1,3,5-tricarboxylic acid crystal structure consists of hydrogen bonded complex [27] and these complexes can be suffered by acetic acid [28]. The copper of carboxylate chemistry is immeasurable and tough because of their remarkable structural facial appearance and properties [29–35]. A balanced drawing and production of coordination polymers are getting extreme attention due to their prospective properties, and also due to their charming outline structures [36–44]. During the few passing years, based on metal ions and rigid spacer ligands like di- or tri-carboxylates coordination polymers have been fruitfully synthesized [45–50]. The chemistry of carboxylic acids finds significance due to effectiveness in number of achievable orientations [51–60] and many kinds in coordination chemistry [61–73]. Due to supra-molecular binding abilities possessed by the organic motifs got the bonus consideration to know their properties in limited means. [74–80].

To the extent of our information no comprehensive work (experimental or theoretical) on the electronic structure and optical properties of 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid has been seen in the literatures. In the present work we used the all-electron full potential linear augmented plane wave (FP-LAPW) method to investigate the electronic structure, optical properties and charge density. The FP-LAPW has been proven to be one of the most accurate methods for the computation of electronic structure work of solid with in density functional theory (DFT).



#### **2. METHODOLOGY**

Figure 1. Unit cell structure of 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid.

The metallohybrid carboxylic acid crystal structure has been obtained from the reaction of copper(II)acetate monohydrate with 1,3,5-benzenetricarboxylic acid (TCAH3) in the existence of

pyridine (py) with composition Cu(py)2(TCAH2)2(H2O)2 [81]. The crystal structure of 1,3dicarbomethoxy4,6-benzenedicarboxylic acid has been shown in Fig. 1, which crystallizes in monoclinic having the space group number 14 (P21/c) and the lattice parameters are  $a = 6.9549(16)A^{\circ}$ , b = 8.7676(15)A°, c = 20.111(4)A° and V = 1225.1(4) A<sup>3</sup> of a unit cell. We got the crystallographic data in the form of CIF, deposited in Cambridge Crystallographic database which has the CCDC number 630337. We have performed the calculation by using all electrons full potential linear augmented plane wave (FP-LAPW) method to resolve Kohn sham DFT equation within the support of the WEIN2K code [82]. This is an accomplishment of the DFT [83] with different feasible approximation for the exchange co-relation. By using the local density approximation, Generalized Gradient Approximation (GGA) and modified Becke–Johnson (mBJ) we have calculated the exchange co-relation (Exc) [84]. This has been recognized that in the self consistent band structure calculation within density functional theory approaches that GGA and LDA usually under estimates the energy gap valve [85]. This is because they are simplified model assumptions which are not suitably elastic to exactly reproduce Exc energy. This shortcoming was overcome by modified Becke–Johnson (mBJ) [86]. Which are capable of having better energy gap. The mBJ yields an improved band splitting compared to LDA and GGA.

In this correspondence, we scrutinize the electronic structure, charge density and optical properties by using density functional theory (DFT). From this work we will be aware of the structural and optoelectronic nature of this compound. The optical properties are frequently discussed in the expressions of the complex dielectric function i.e.  $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$ . The dielectric function imaginary part in the long wavelength limit has been got from the electronic structure calculation by making the use of the joint density of states (DOS) and the optical matrix elements. While the dielectric functions real part is calculated from the imaginary part by using the relationship of Kramer's-Kronig.

#### **3. RESULTS AND DISCUSSION**

### 3.1 Band Structure

The calculated electronic band structure along the symmetry points is shown in Fig 2. It can be clearly seen that, the top of the valence band located at the X point and the bottom of the conduction band is located at the  $\Gamma$  point, defining the indirect band gap of 3.93 eV within mBJ, while the band gap for LDA and GGA are 2.99 eV and 3.05 eV respectively. To the best of our knowledge, there are no previous experimental or theoretical data for the energy band gaps available in literature to make a meaningful comparison. Thus, we expect that our band gap value might be lower than the experimental ones, due to DFT underestimation. it is well-known that first-principles calculation of the electronic structure of semiconductors and insulators using LDA and GGA underestimate the band gap values compared to experiments. This underestimation is mainly due to the fact that GGA endures from artificial electron self-interaction and also be deficient in the derivative discontinuities of the

exchange-correlation potential with respect to occupation number. However mBJ approximation used for exact band gap calculations, which is better than LDA and GGA.



Figure 2. Calculated band structure.

#### 3.2 Density of states

In this part we analyze the density of states of the monoclinic 1,3-dicarbomethoxy4,6benzenedicarboxylic acid. We calculated the total and partial density of states (DOS) of the investigated compound using LDA, GGA and mBJ schemes. From the density of states we can analyze the electronic band gap nature. From the eigenvalues and eigenvectors solved at sufficient number kpoints in the BZ, the total DOS can be projected into its partial components (PDOS) with respect to the different atoms. Fig. 3 shows the calculated total and partial densities of states for 1,3dicarbomethoxy4,6-benzenedicarboxylic acid. The density of states (DOS) can be divided into two groups/structures which are separated by gaps. From the PDOS we are capable to classify the angular momentum (*l*-dependent) origin of the different bands.

Following Fig. 3, the peaks from -11.0 and -9.0 eV is due to the contribution of C-s and O-p states. The peaks between -8.0 and -1.0 eV consist of O-p, C-p and H-s in states. In the conduction bands the peaks situated in the region between 4.0 eV and 8.0 eV consist of mainly C-p and from 9.0

eV and 20.0 eV consist of H-s and C-s/p. There exists a strong hybridization between C-p and H-s states in the energy range between -8.0 eV and 4.0 eV.





Figure 3. Calculated total and partial densities of states (States/eV unit cell)



3.3 Electron Density





**(e)** 

Figure 4. Electronic charge density contour in (101) plane (a) LDA (b) GGA (c) EV-GGA

To further study the interaction among C, H and O atoms, the contour maps of electron densities for LDA, GGA and mBJ in the 2D (101) plane and also the (111) plane for mBJ are plotted in Figs. 4. The plot is ionic and partial covalent bonding between C and O, which acting on the Pauling electro-negativity difference of C (2.55) and O (3.44) atoms. The calculated electron density shows that charge density lines are spherical in some areas of the plane structure which shows sign of ionic bond between O atoms and in some areas of structures C and O atoms shared electron that shows the strong covalent interaction between C - O, O - H and C - H. Due to the electro negativity differences between C, O, and H atoms, thus most the charges are transferred to O site. This can be seen straightforwardly by color charge density scale, where blue color (+1.000) corresponds to the utmost charge gather ion site. The contact between C and O produces covalent-like bond due to small electronegativity difference around (0.89). So 1,3-dicarbomethoxy 4,6-benzenedicarboxylic acid has both ionic and covalent bond. The electronic charge density between H – O and C – H shows weak covalent bonding. The plot in the different plane shows the variation in the electronic charge density as shown in Fig.4. In the (111) plane the bond between C-C shows strong ionic and weak covalent bonding, while in the (101) plane it shows completely covalent bond, labeled as 1 in Fig.4 (e). As O shows the ionic bonding in both plane, in (101) plane the charge density around O site distributed in is circular form, whereas in (111) plane the charge density distribution take the shape of dumbbell as labeled 2 in Fig.4 (e).

## 3.4 Optical properties

The structure of 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid crystallizes in the monoclinic. Normally there are two types of involvement to frequency dependent dielectric function namely intra and inter band transition. The contribution due to intra band transition is only for metals. The dielectric function  $\varepsilon_2(\omega)$ , inter-band transitions can become apart to direct and indirect transitions. We overlook the indirect inter-band transitions which linking scattering of phonons that are predictable to give a small contribution to ( $\varepsilon_2(\omega)$ ). For calculating the direct inter band contribution of the dielectric function  $\varepsilon_2(\omega)$ , this is fundamental to calculate all achievable transition occurring in occupied and unoccupied states which take the correct transition matrix elements in description. In the long wavelength limit the imaginary part is obtained directly from electronic structure calculation by means of the joint density of states and transition moments elements [87];

$$\varepsilon_{2}^{ij}(\omega) = \frac{8\pi^{2}\hbar^{2}e^{2}}{m^{2}V} \sum_{k} \sum_{cv} (f_{c} - f_{v}) \frac{p_{cv}^{i}(k)p_{vc}^{j}(k)}{E_{vc}^{2}} \delta[E_{c}(k) - E_{v}(k) - \hbar\omega]$$

Where *m*, *e* and  $\hbar$  denotes the electron mass, charge and Plank's constant, respectively and  $f_c$  and  $f_v$  symbolize the Fermi distributions of the conduction and valence bands. The expression  $p_{cv}^i(k)$  denotes the momentum matrix element transition of energy from the level *c* of the conduction band to the level *v* of the valence band at certain **k**-point in the BZ and *V* is the unit cell volume.

Our calculated result of imaginary (absorptive) and real (dispersive) parts of the dielectric functions is displayed in Fig.5a and b using LDA, GGA and mBJ.



**Figure 5.** Calculated imaginary  $\varepsilon_2(\omega)$  and real part  $\varepsilon_1(\omega)$  of dielectric tensor

We should emphasize that mBJ gives rise to a better band splitting, resulting in better optical transition between the occupied and unoccupied states. So for this motive we discuss the result of mBJ. Following Fig. 5, one can see that all the structure is shifted towards higher energies by around 0.5 eV with higher magnitude especially for the spectral structure at lower energies. A number of irrelevant humps are seen between these structures in these three components. We should emphasize that there is a considerable anisotropy between the three schemes.

We preview the optical spectra for the energy range 0.0–14.0 eV. Fig. 5 a, shows that the whole structure is shifted towards higher energies by around 0.5 eV with higher magnitude especially for the first spectral structure at lower energies.

By ensuing the spectra of  $\varepsilon_2(\omega)$ , the highest spectral peak for the three schemes LDA, GGA and mBJ are situated at energies 3.68 eV, 3.73 eV and 4.42 eV respectively. From the imaginary part  $\varepsilon_2(\omega)$ , the real part  $\varepsilon_1(\omega)$  was calculated using the kramers-kronig equation [88], the real part has the peaks at energies 3.35 eV, 3.45 eV and 4.05 eV for LDA, GGA and mBJ, respectively as shown in Fig. 5 b.

In solid the optical properties are account by dielectric tensor. The investigated crystals have monoclinic symmetry, which has many nonzero components of the second-order dielectric tensor. In regardless of this only  $\varepsilon_2^{xx}(\omega)$ ,  $\varepsilon_2^{yy}(\omega)$  and  $\varepsilon_2^{zz}(\omega)$  are major, these are the imaginary parts of the frequency-dependent dielectric function. Fig. 6a, illustrates the calculated imaginary part of the anisotropic frequency-dependent dielectric functions. Broadening has been assumed to be 0.1 eV which is normal for the broadening starting from the electron-phonon interactions. We noticed that  $\varepsilon_2^{zz}(\omega)$  and  $\varepsilon_2^{yy}(\omega)$  shows the major contribution with adequate anisotropy with  $\varepsilon_2^{xx}(\omega)$  component.





**Figure 6.** Calculated average value of imaginary and real part of dielectric function (a)  $\varepsilon_2^{av}$  (b)  $\varepsilon_1^{av}$ 

There is considerable anisotropy between the three spectrum corresponding to different polarization for this compounds and its maximum valves are at 4.17 eV, 5.44 eV and 4.14 eV for  $\varepsilon_2^{xx}(\omega)$ ,  $\varepsilon_2^{yy}(\omega)$  and  $\varepsilon_2^{zz}(\omega)$ , respectively. Apart from the main peaks the next structure peaks are at 5.19 eV for  $\varepsilon_2^{xx}(\omega)$ , 4.06 eV for  $\varepsilon_2^{yy}(\omega)$  and 5.49 eV for  $\varepsilon_2^{zz}(\omega)$ . The peaks that emerge in the Fig. 6a, communicate to energy transitions between some orbital corresponding to certain energy because  $\varepsilon_2(\omega)$  is narrated to the DOS. In comparison with Fig. 6a, it can be recognized that the peaks are mainly due to the transition from the occupied O-2p to unoccupied C-2p or H-1s. From the dielectric functions  $\varepsilon_2^{xx}(\omega)$ ,  $\varepsilon_2^{yy}(\omega)$  and  $\varepsilon_2^{zz}(\omega)$  the real parts  $\varepsilon_1^{xx}(\omega)$ ,  $\varepsilon_1^{yy}(\omega)$  and  $\varepsilon_1^{zz}(\omega)$  were calculated. The results of  $\varepsilon_1^{xx}(\omega)$ ,  $\varepsilon_1^{yy}(\omega)$  and  $\varepsilon_1^{zz}(\omega)$  are shown in Fig. 6b.

Using  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$ , we have calculated the related optical properties, namely the energyloss spectrum L( $\omega$ ), reflectivity R( $\omega$ ) and the refractive index n( $\omega$ ) as shown in Figure 7. The electron energy loss spectroscopy is a valuable tool for investigating various aspects of materials [90]. The energy-loss spectrum is related to the energy loss of a fast Electron traversing in the material and is usually large at the plasma energy [91]. The plasmon losses correspond to a collective oscillation of the valence electrons and their energies are related to the density of valence electrons. In the case of inter-band transitions, which consist mostly of plasmon excitations, the scattering probability for volume losses is directly connected to the energy loss function. The frequency corresponding to the plasma resonance can be calculated from the energy loss spectrum shown in Fig. 7a. The most prominent peak in the energy-loss spectrum is identified as the plasmon peak and located at 6.20 eV

for  $L^{xx}(\omega)$  and 13.54  $L^{yy}(\omega)$  and  $L^{zz}(\omega)$ . The peaks in each of these spectra correspond to the peaks observed in the imaginary part  $\varepsilon_2(\omega)$  of dielectric function.





**Figure 7.** Calculated energy-loss spectrum  $L(\omega)$ , reflectivity  $R(\omega)$  and the refractive index  $n(\omega)$ 

Fig. 7b shows the variations of reflectivity  $R(\omega)$  of 1,3-dicarbomethoxy4,6benzenedicarboxylic acid in the energy range of 0–14 eV. It is interesting to note a continuous abrupt increased and reduction in the reflectivity spectrum which confirming the occurrence of a plasmon resonance. The plasmon minimum depth is determined by the imaginary part of the dielectric function at the plasma resonance and is the envoy of the degree of overlap between the interband absorption regions. The zero-frequency reflectivity remains almost the same up to 2 eV. After 2 eV it increases and eventually becomes maximum. The most prominent peaks are observed at 5.60 eV, 5.57 eV and 4.14 eV for  $R^{xx}(\omega)$ ,  $R^{yy}(\omega)$  and  $R^{zz}(\omega)$  respectively. Interestingly, at 4.30 eV the maximum reflectivity occurs where the  $\varepsilon_1(\omega)$  goes below zero, as seen from Figs. 7b and 6b.

The refractive index of a crystal is closely related to the electronic polarizability of ions and the local field inside the crystal. The values of n(0) are found to be 1.39, 1.30 and 1.32 along  $n^{xx}(\omega)$ ,  $n^{yy}(\omega)$  and  $n^{zz}(\omega)$  respectively. It is clear that the refractive index increases from its zero frequency limit and reaches the maximum value of 4.07 for  $n^{xx}(\omega)$  and 3.96 for both  $n^{yy}(\omega)$  and  $n^{zz}(\omega)$  at around 4.0 eV, as exposed in Fig. 7c. Beyond the maximum value it starts decreasing and goes below unity after 4.29 eV. Refractive index less than unity  $\left(v_g = \frac{c}{n}\right)$  shows that the group velocity of the

incident radiation is greater than c [89]. This signifies that the group velocity moves to negative domain and the character of medium changes from linear to nonlinear. And the material becomes superluminal for high energy photons.

## **4. CONCLUSION**

The structure of 1,3-dicarbomethoxy 4,6-benzenedicarboxylic acid was optimized by minimizing the forces acting on each atom. Then we provide detailed calculation on the electronic structure and linear optical properties of the 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid by means of the full potential linear augmented plane wave (FPLAPW) method within LDA, GGA and mBJ. The total and partial densities of states, as well as optical properties, were analyzed. The calculation show that the compound is

indirect band gap material (X- $\Gamma$ ) of about 2.99, 3.05 and 3.93 eV for LDA, GGA and mBJ respectively. Even though there exist no experimental or theoretical calculations with which we should compared our results, obviously, the top of our analyzed studies prove the consistency of our calculations, signifying that calculations should be realistic for the 1,3-dicarbomethoxy4,6-benzenedicarboxylic acid. We studied the electronic charge density in the (1 1 0) crystallographic plane in order to explain the bonding properties. The dielectric optical properties were also calculated and discussed in detail.

#### AKNOWLEDEGMENT

This work was supported from the project CENAKVA (No. CZ.1.05/2.1.00/01.0024), the grant No. 134/2013/Z/104020 of the Grant Agency of the University of South Bohemia. School of Material Engineering, Malaysia University of Perlis, P.O Box 77, d/a Pejabat Pos Besar, 01007 Kangar, Perlis, Malaysia

## References

- 1. M. S. Refat, S. A. El-Korashy, D. N. Kumar, A. S. Ahmed, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 70 (2008)898–906
- 2. S. Mandal, G. Rosair, J. Ribas, D. Bandyopadhyay, *Inorg Chim Acta* 362 (2009) 2200–2204.
- 3. G. Venkatachalam, N. Raja, D. Pandiarajan, R. Ramesh, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 71 (2008) 884–891
- 4. T. Z. Yu, K. Zhang, Y. L. Zhao, C. H. Yang, H. Zhang, D. W. Fan, W. K. Dong, *Inorg Chem Commun*, 10 (2007) 401–403
- 5. P. Mukherjee, C. Biswas, M. G. B. Drew, A. Ghosh, Polyhedron, 26 (2007) 3121-3128
- 6. S. Chattopadhyay, G. Boclli, A. Musatti, A. Ghosh, Inorg Chemi Commun, 9 (2006) 1053–1057
- 7. L. T. Yidirim, R. Kurtaran, H. Namli, A.D. Azaz, O. Atakol, Ployhedron, 26 (2007) 4187–4194
- 8. K. C. Gupta, A. K. Star, *Coord Chem Rev*, 252 (2008) 1420–1450
- H. Eshtiagh-Hosseinia, M. R. Housaindokhta, S. A. Beyramabadia, S. Beheshtia, A. A. Esmaeilib, M. K. Khoshkholghb, A. Morsalic, *Spectrochimica Acta Part* A, 71 (2008) 1341–1347
- E. Keskioglu, A. B. Gunduzalp, S. Cete, F. Hamurcu, B. Erk, Spectrochimica Acta Part A, 70 (2008) 634–640
- 11. C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, Angew Chem Int Ed, 43 (2004) 1466
- 12. M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. Keeffe, O. M. Yaghi, *Acc Chem Res*, 34 (2001) 319
- 13. B. Moulton, M. J. Zaworotko, Chem Rev, 101 (2001) 1629
- 14. S. L. James, Chem Soc Rev, 32 (2003) 276
- 15. R. Murugavel, M.G. Walawalkar, M. Dan, H. W. Roesky, C. N. R. Rao, *Acc Chem Res*, 37 (2004) 763

- 16. K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab, V. V. Pavlishchuk, *J Am Chem* Soc, 127 (2005) 12247
- 17. M. Casarin, C. Corvaja, C. D. Nicola, D. Falcomer, L. Franco, M. Monari, L. Pandolfo, C. Pettinari, F. Piccinelli, *Inorg Chem*, 44 (2005) 6265
- 18. M. Eddaoudi, H. Li, O. M. Yaghi, J Am Chem Soc, 127 (2005) 7110
- 19. M. J. Platers, R. A. Howie, A. Roberts, J Chem Commun, (1997) 893
- 20. P. K. Chen, Y. X. Che, J. M. Zheng, Jiegou Huaxue, 25 (2006) 1427
- 21. C. Serre, F. Millange, S. Surble, G. Ferey, Angew Chem Int Ed, 43 (2004) 6286
- 22. D. E. Lynch, G. Smith, K. A. Byriel, C. H. L. Kennard, Aust J Chem, 45 (1992) 835
- 23. M. Du, Z-H. Zhang, X-J. Zhao, Cryst Growth Des, 5 (2005) 1247
- 24. H. S. Huh, D. Min, Y. K. Lee, S. W. Lee, Bull Korean Chem Soc, 23 (2002) 619
- 25. N. Feedrer, W. Jones, Acta Crystallogr C, 50 (1994) 820
- 26. N. Barooah, R. J. Sarma, A. Batsanov, J. B. Baruah, J Mol Struct, 791 (2006) 122
- 27. D. J. Duchamp, R. E. Marsh, Acta Cryst Sec B, 25 (1969) 5
- 28. I. Goldberg, Bernstein, J Chem Commun, 132 (2007)
- 29. R. E. Del Sesto, A. M. Arif, J. S. Miller, Inorg Chem 39 (2000) 4894
- 30. O. Kahn, Chem Phys lett, 265 (1997) 109
- 31. M. Kato, Y. Muto, Coord Chem Rev, 92 (1988) 45
- 32. S. Ferrer, F. Lioret, I. Beertmenu, G. Alzuet, J. Borras, S. Garcia- Granda, M. Liu-Gonzales, J. G. Hassnoot, *Inorg Chem.* 41 (2002) 5821
- G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb, D. N. Hendrickson, Inorg Chem, 29 (1990) 3657
- 34. L. Porter, R. Doedens, Inorg Chem, 24 (1985) 1006
- 35. S. M-F. Lo, S. S-Y. Chui, L. Y. Shek, Z. Lin, X. X. Zhang, G. H. Wen, I. D. Williams, *J Am Chem Soc*, 122 (2000) 6293
- 36. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705
- N. L. Rosi, J. Eckert, M. Eddaoudi, D. V. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science*, 300 (2003) 1127
- R. G. Xiong, X. Xue, H. Zhao, X. Z. You, B. F. Abrahams, Z. L. Xue, Angew Chem Int Ed, 41 (2002) 3800
- 39. B. Moulton, J. J. Lu, R. Hajndl, S. Harkkharan, M. J. Zaworotko, *Angew Chem Int. Ed*, 41 (2002)2821
- 40. K. Seki, W. Mori, J Phys Chem B, 106 (2002) 1380
- 41. S. Kitagawa, R. Kitaura, S. Noro, Angew Chem Int Ed, 43 (2004) 2334
- 42. P. J. Hagrman, D. Hagrman, J. Zubieta, Angew Chem Int Ed, 38 (1999) 2638
- 43. J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, Nature 404 (2000) 982
- 44. G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* 309 (2005) 2040
- 45. M. Eddaoudi, J. Kim, N. Rsi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* 295 (2002) 469
- 46. B. Chen, N. W. Ockwig, F. R. Fronczek, D. S. Contreras, O. M. Yaghi, Inorg Chem, 44 (2005)181
- 47. X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa, S. R. Batter, Angew Chem Int Ed, 43 (2004)192
- 48. S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science*, 283 (1999) 1148
- 49. S. J. Lee, A. Hu, W. Lin, J Am Chem Soc, 124 (2002) 12948
- 50. C. J. Kepert, T. J. Prior, M. J. Rosseinsky, J Am Chem Soc, 122 (2000) 5158
- 51. M. Du, Z-H. Zhang, X-J. Zhao, H. Cai, Cryst Growth Des, 6 (2006) 114
- 52. A. M. Beatty, C. M. Schneider, A. E. Simpson, J. L. Zaher, Cryst Eng Comm, 4 (2002) 282
- 53. M. Du, Z-H. Zhang, X. Zhao, J Cryst Growth Des, 6 (2006) 335
- 54. V. R. Pedireddi, S. Chaterjee, A. Ranganthan, C. N. R. Rao, Tetrahedron, 54 (1998) 9457

- 55. J. Xiao, M. Yang, J. W. Lauher, F. W. Fowler, Angew Chem Int Ed, 39 (2000) 2132
- 56. C. B. Aakero"y, A. M. Beatty, B. A. Helfrich, M. Niuwenhuyzen, Cryst Growth Des, 3 (2003) 159
- 57. P. Vishweshwar, A. Nangia, V. M. Lynch, Cryst Growth Des, 3 (2003) 783
- 58. D. Braga, L. Maini, G. Sanctis, K. Rubini, F. Grepioni, M. R. Chierotti, R. Gobetto, *Chem Eur, J* 9 (2003) 5538
- 59. D. Singh, P. Bhattacharyya, J. B. Baruah, Crystal Growth Des, 10 (2010) 348
- 60. N. Barooah, R. J. Sarma, J. B. Baruah, Cryst Eng Comm, 8 (2006) 608
- 61. A. Erxleben, Coord Chem Rev, 246 (2003) 203
- 62. A. J. Fletchera, K. M. Thomasa, M. J. Rosseinsky, J Solid State Chem, 178 (2005) 2491
- 63. K. Uemura, R. Matsuda, S. Kitagawa, J Solid State Chem, 178 (2005) 2420
- 64. F. S. Delgado, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, Crys Eng Comm, 6 (2004) 73
- 65. F. S. Delgado, M. Hernandez-Molina, J. Sanchiz, C. Ruiz-Perez, Y. Rodriguez-Martin, T. Lopez, F. Lloret, M. Julve, *Cryst Eng Comm*, 6 (2004) 929
- 66. I. GildeMuro, L. Lezama, M. Insausti, T. Rojo, Polyhedron, 23 (2004) 859
- 67. F. S. Delgado, C. Ruiz-Perez, J. Sanchiz, F. Lloret, M. Julve, Cryst Eng Comm 8 (2006) 530
- 68. J. Pasan, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, Inorg Chem, 44 (2005) 7794
- 69. P. Lightfoot, A. Snedden, JCS Dalton Trans (1999) 3549
- 70. Y. Rodriquez-Martin, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, *Cryst Eng Comm*, 4 (2002) 631
- 71. P. Mondal, A. Karmakar, W. M. Singh, J. B. Baruah, Cryst Eng Comm, 10 (2008) 1550
- 72. A. Karmakar, J. B. Baruah, R. B. Shankar, Cryst Eng Comm, 11 (2009) 832
- 73. O. M. Yaghi, M. O'keefe, N. W. Ockwig, H. K. Chae, M. Eddaoudi M, J. Kim, *Nature*, 423 (2003) 705
- 74. A. Heller, B. Feldman, Chem Rev, 108 (2008) 2482
- 75. Aubart KM, Heathcock CH (1999) J Org Chem 64:16
- 76. Y. Huang, J. Zhang, T. R. R. Pettus, Org Lett, 7 (2005) 26
- 77. J. K. Liu, Chem Rev, 106 (2006) 2209
- 78. V. K. Tandon, H. K. Maurya, D. B. Yadav, A. Tripathi, M. Kumar, P. K. Shukla, *Bioorg Med Chem Lett*, 16 (2008)5883
- 79. J. Benites, L. Rojo, J. A. Valderrama, H. Taper, P.B. Calderon, Eur J Med Chem, 43 (2008)1813
- 80. K. O. Eyong, P. S. Kumar, V. Kuete, G. N. Folefoc, E. A. Nkengfack, S. Baskaran, *Bioorg Med Chem Lett* 18 (2008) 5387
- 81. C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, Angew Chem Int Ed, 43 (2004) 1466
- 82. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, WEIN2K, an augmented plane wave + local orbitals programme for calculatingcrystal properties; Technische Universitat, Wein: Vienna, Austria, (2001) ISBN 3-9501031-1-2.
- 83. P. Hohenberg, W. Kohn, phys. Rev, B, 136 (1964) 864s
- 84. F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401.
- 85. P. Dufek, P. Balaha, K. Schwarz, Phy, Rev. B, 50 (1994) 7279.
- 86. E. Engel, S. H. Vosko, Exact exchange-only potential and the virial relation as microscopic criteria for generalized gradient approximations, *Phys. Rev.* B, 47 (1993) 13164-13174.
- 87. A. Delin, P. Ravindran, O. Eriksson, J.M. Wills, Int. J. Quant. Chem. 69, 349(1998).
- 88. F. Wooten, Optical properties of solids. (1972) Academic Press, New York.
- 89. L. J. Wang, A. Kuzmich, A. Dogariu, Nature, 406 (2000) 277
- 90. S. Loughin, R.H. French, L.K. De Noyer, W.-Y. Ching, Y.-N. Xu, J. Phys. D: Appl.Phys. 29 (1996) 1740.
- 91. P. Nozieres, Phys. Rev. Lett. 8 (1959) 1.

© 2013 by ESG (<u>www.electrochemsci.org</u>)