Electronic Supplementary Material (ESI) for RSC Advances.

Appendix A: Supporting Information

Novel cobalt (II) acetate complex bearing lutidine ligand: A promising electrocatalyst for oxygen evolution reaction

Deepika Tanwar[a,b#], Priya Jain[c#], Deepali Ahluwalia[d], Athul Sudheendranath[c], Sajesh P. Thomas[c], Pravin P. Ingole[c]*, Umesh Kumar[a]*

[a]*Catalysis and Bioinorganic Research Lab, Department of Chemistry, Deshbandhu College, University of Delhi, New Delhi-110019, India.*
[b]*Department of Chemistry, University of Delhi, New Delhi-110007, India.*
[c]*Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India.*
[d]*Department of Applied Chemistry, Delhi Technological University, New Delhi-110042, India.*
[#]*Equally Contributed*

Email: ppingole@chemistry.iitd.ac.in, ukumar@db.du.ac.in

1. Materials and Methods

All chemicals were purchased from commercial vendors and used without further purification. The solvents were distilled using drying agents before use. The IR spectral data for samples were obtained using an IR Affinity–1 Shimadzu FTIR spectrometer from powdered samples by ATR method and on a Shimadzu IR435 spectrometer using KBr pellets and data are presented in the frequency range 400–4000 cm^{-1}. Elemental analyses were analyzed on ElementarAnalysenSysteme GmbH VarioEL V3.00.The morphology and microstructures were characterized by using field-emission scanning electron microscopy (FESEM) using Zeiss EVO-50 instrument. The EDX elemental mapping was performed by RONTEC's EDX system Model QuanTax 200. Raman spectroscopy was performed using confocal laser Raman microscope (Renishaw, UK) using the laser of 514 nm wavelength.

1.1 X-ray Diffraction Studies

Single crystal XRD data for complex **1** was collected on Oxford Xcalibur S diffractometer (4-circle kappa goniometer, Sapphire-3 CCD detector, omega scans, graphite monochromator, and a single wavelength Enhance X-ray source with MoKα radiation).[1] Pre-experiment, data collection, data reduction, and absorption corrections were performed with the CrysAlisPro software suite.[2] The structure was solved and refined using the *SIR* 2004 and SHELX-2017 program package, respectively (within the Olex2 program package).[3-5] Non-hydrogen atoms were refined anisotropically. C−H hydrogen atomswere refined using a riding model. Solvent masking was attempted to model any solvent molecules that may be potentially occupying the crystal voids.

However, it did not result in any significant improvement in the residual electron density features or refinement parameters, and hence the solvent mask model was discarded. The crystal structure diagrams were created using Diamond software.[6] The non-covalent interactions and voids were analyzed using Mercury software. Crystallographic data are given in Table S1.

1.2 Computational Methods

The structures obtained from X-ray crystallographic analysis were subjected to theoretical calculations by employing density functional theory (DFT) method. The geometry of complex **1** was optimized under C1 symmetry at B3LYP functional using LANL2DZ as basis set.[7-9] In order to understand the electron density distribution within the complex **1**, the frontier molecular orbitals were visualized. All the calculations have been performed in Gaussian 09W suits of program.[10,11] All the molecular images were generating using GaussView 5.0. The studies of the molecular electrostatic potential surfaces have also been incorporated in the present work, using these optimized geometries. The studies of non-covalent interactions (NCI) have also been incorporated in this work, using Multiwfn 3.8 software.[12] The isosurfaces were visualized with the help of VMD 1.9.4a51 version.[13] The two-dimensional colored reduced density plots have been mapped using gnuplot 5.4 software.[14]

Table 1: Crystallographic and experimental parameters for complex **1.**

Identification code	ACETRONITRIL (Co-complex **1**)
Empirical formula	$C_9H_{14}Co_{0.5}NO_3$
Formula weight	213.68
Temperature/K	293(2)
Crystal system	trigonal
Space group	R-3
a/Å	24.7312(8)
b/Å	24.7312(8)
c/Å	9.5600(3)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5063.8(4)
Z	18
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	0.794
F(000)	2025.0
Crystal size/mm^3	0.25 × 0.2 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.078 to 59.386
Index ranges	$-33 \leq h \leq 34$, $-32 \leq k \leq 31$, $-13 \leq l \leq 12$
Reflections collected	26334
Independent reflections	2977 [R_{int} = 0.0347, R_{sigma} = 0.0223]
Data/restraints/parameters	2977/0/129
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0347, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.0933
Largest diff. peak/hole / e Å^{-3}	0.70/-0.28

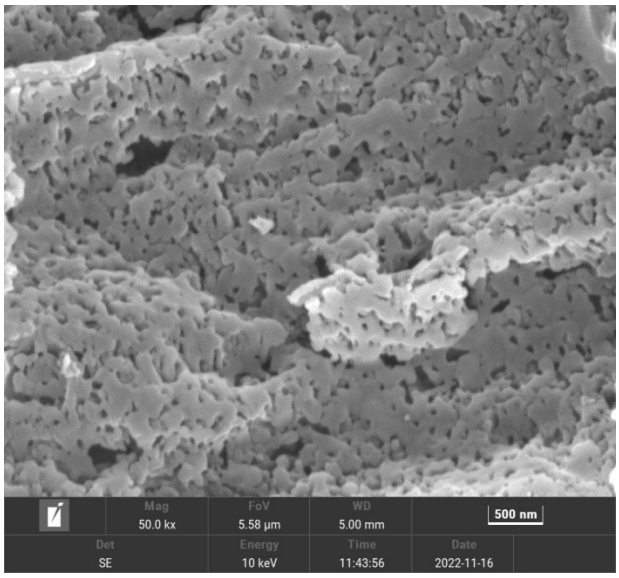


Figure SI-1: The FESEM image of Co complex **1** with scale bar 500nm**.**

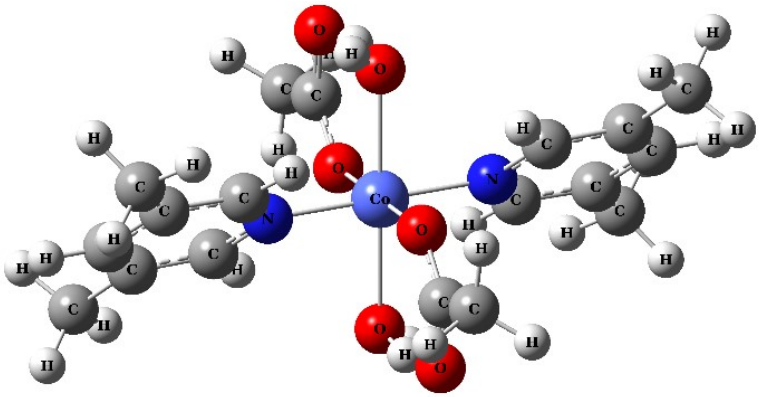


Figure SI-2: Optimized geometries of complex **1** obtained from DFT calculations.

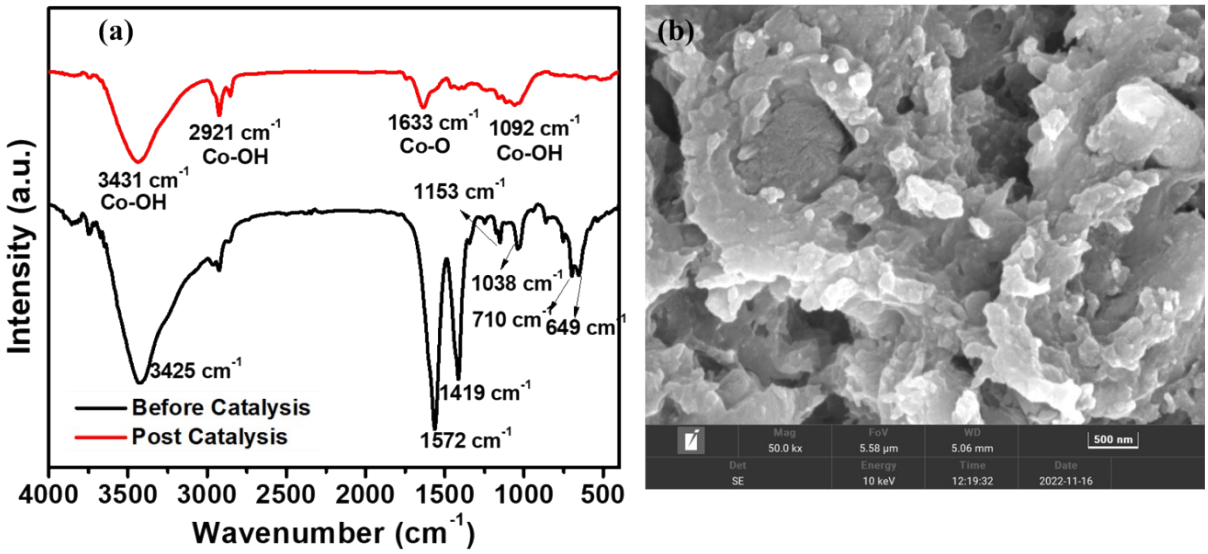
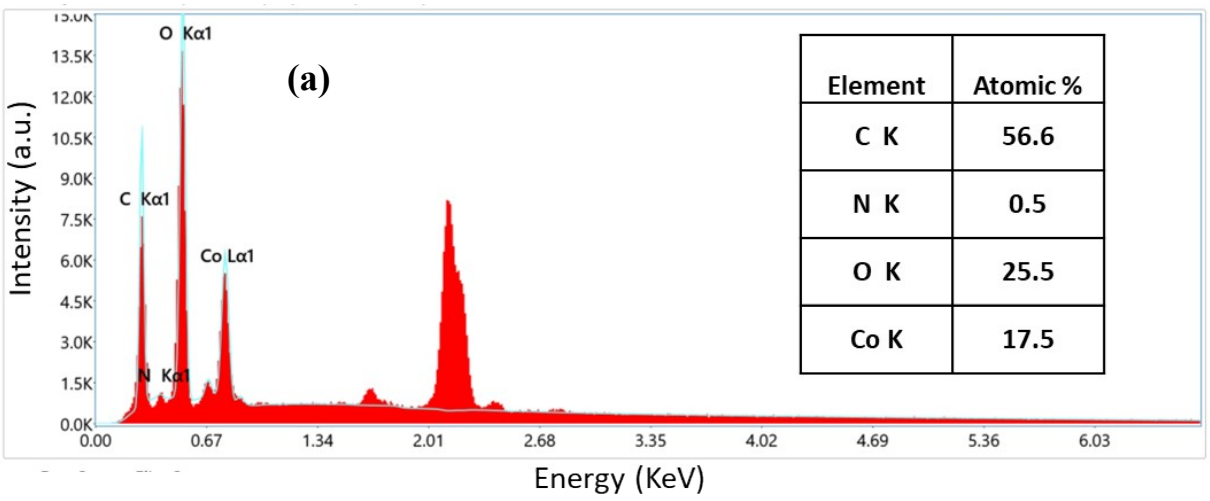


Figure SI-3: a) The pre and post catalytic FTIR and b) post catalytic FESEM image for Co-complex (**1**).



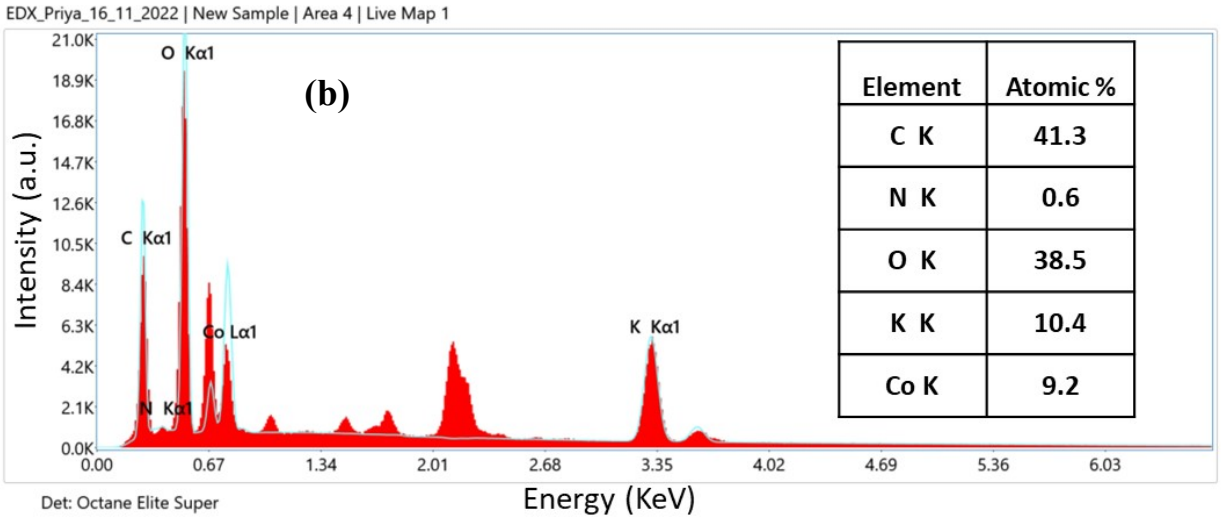
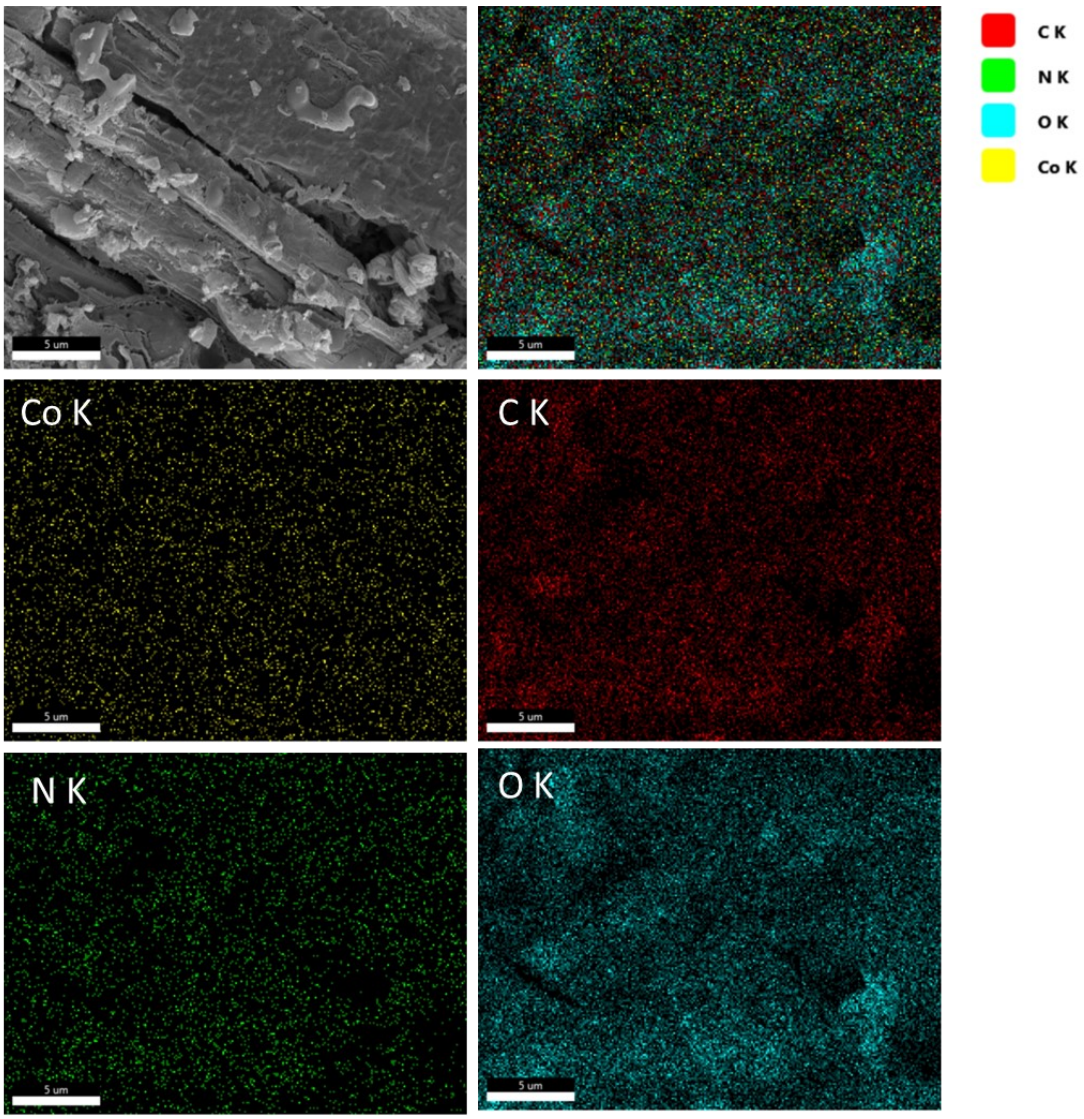


Figure SI-4: Energy dispersive X-ray spectra of Co-complex (**1**) **(a)** before and (**b)** after OER catalysis.

(a)



(b)

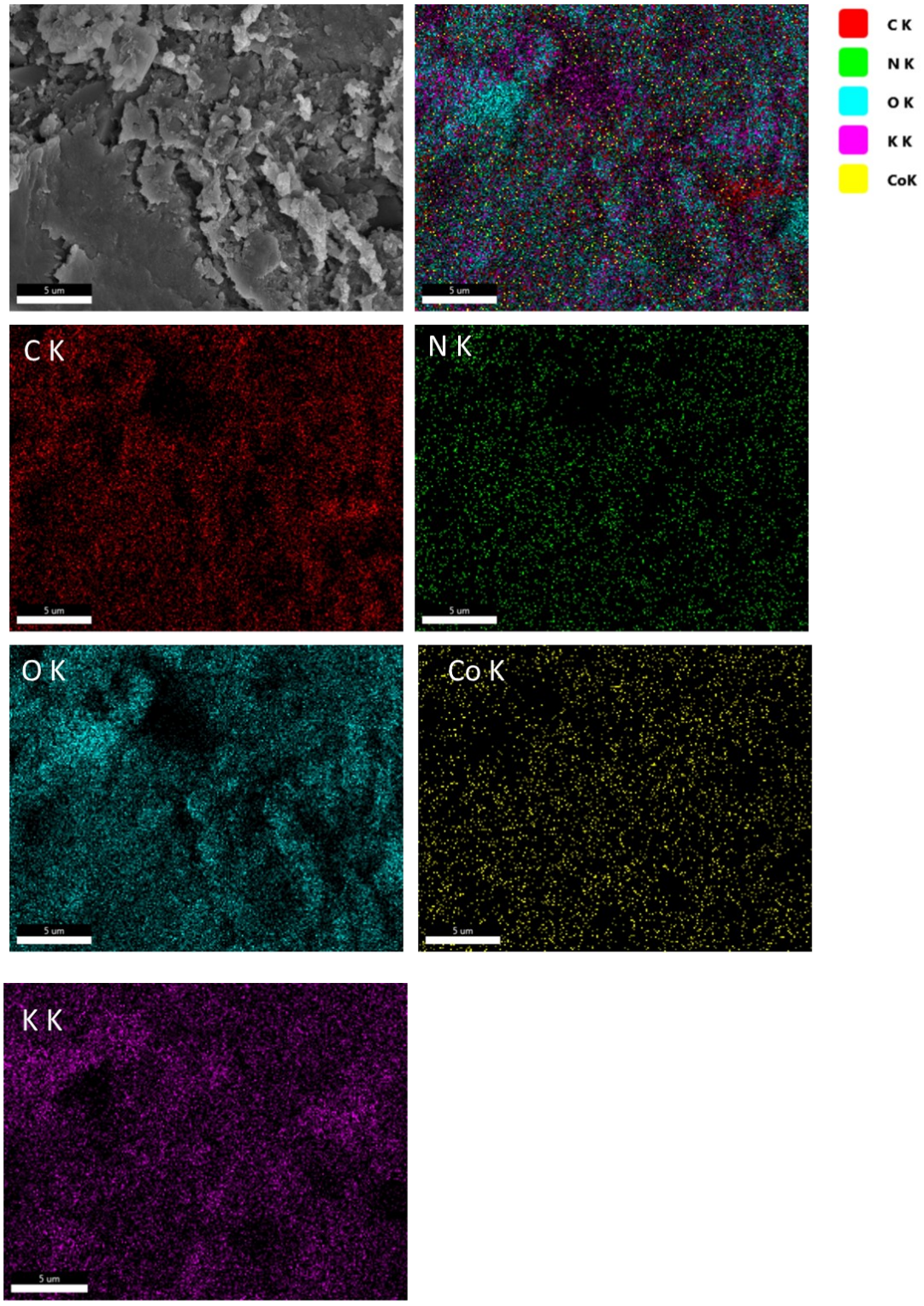


Figure SI-5: Elemental mapping of Co-complex (**1**) a) before and b) after catalysis

References

1. ENHANCE, Oxford Xcalibur Single Crystal Diffractometer, version 1.171.34.49, Oxford Diffraction Ltd: Oxford, U.K., 2006.
2. CrysAlisPro, version 1.171.34.49, Oxford Diffraction Ltd: Oxford, U.K., 2011.
3. G. M. Sheldrick, SHELXS-97 and SHELXL-97, program for crystal structure solution and refinement,University of Gottingen, Gottingen, Germany, 2017.
4. A. Altomare, G. Cascarano, C.Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *SIRPOW*.92 – a program for automatic solution of crystal structures by direct methods optimized for powder data. *J. Appl. Crystallogr.* 1994, **27***,* 435-436.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H.Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, **42**, 339-341.
6. H. Putz and K. B.GbR, Diamond-crystal and molecular structure visualization crystal impact, Kreuzherrenstr, 102, 53227 Bonn, Germany.
7. W. J. Hehre, R. Ditchfieldand J. A. Pople,*J. Chem. Phys*.,1972, **56,** 2257-2261.
8. W. R. Wadt, P. J. Hay,*J. Chem. Phys.*, 1985,**82**, 270-285.
9. S. Chiodo, N. Russo and E. Sicilia,*J. Chem. Phys.*, 2006, **125**, 104107-10416.
10. A. D. Becke, *J. Chem. Phys.*1993, **98**, 5648-5652.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G.Scalmani, V. Barone, B.Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.Hratchian, A. F.Izmaylov, J.Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro,

M. Bearpark, J. J.Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N.Rega, J. M.Millam, M.Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R.Cammi, C. Pomelli, J. W.Ochterski, R. L. Martin, K.Morokuma, V. G.Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S.Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowskiand D. J. Fox (2010) Gaussian, Inc., Wallingford CTGaussian 09, revision B.01.

12. T. Lu and F. Chen, *J. Comput. Chem.*, 2011, **33**, 580-592.
13. W. Humphrey, A. Dalke and K. Schulten, VMD: Visual molecular dynamics,*J. Mol. Graph.*, 1996,**14**, 33-38.
14. T. Williams, Kelly Cgnuplot 5.4 An Interactive Plotting Program.