

Preface

The 4th International Conference on Functional Materials Science 2018 (ICFMS 2018) was international conference for promoting collaborative research program on physical and chemical studies of functional materials under the collaboration between Indonesian researchers and some researchers from institutions/universities in Asia and Europe, held in Bali, Indonesia, November 13-15, 2018. It was jointly organized by Institut Teknologi Bandung, Universitas Padjadjaran, Institut Teknologi Sepuluh November, Universitas Gadjah Mada, Universitas Indonesia, and RIKEN Nishina Center, Japan.

Our first conference held in Bali on April 27-28, 2011, successfully gathered researchers from 14 universities in Indonesia and 10 institutions/universities in Asia and Europe. Our second conference held in Lombok on November 12-13, 2014, also successfully gathered researchers from more universities and institutions in Asia and Europe. The third conference held in Bali on October 19-20, 2016, also successfully gathered researchers from more universities and institutions in Asia and Europe.

For the 4th ICFMS 2018, more than 120 papers were presented in both oral and poster presentation in various scopes including (1) Advanced and Functional Materials, (2) Materials and Devices, (3) New Materials for Energy and Energy Conversion (4) Biomaterials, (5) Theoretical/Modeling/Computer Simulations of Functional Materials, (6) Spectroscopy for Advanced Materials, (7) Hybrid and Composite Materials, and (8) Magnetic Materials. Each published paper was peer-reviewed by two reviewers for quality ensuring.

In conjunction with 4th ICFMS 2018, we also hosted the 2nd RIKEN Symposium, which was a continuation of the successfully previous 1st event in the frame of “International Workshop on Organic Molecule Systems” held in Penang, Malaysia, 2017, in collaboration between RIKEN Nishina Center and Universiti Sains Malaysia (USM). This symposium was intended to provide a platform for the exchange of research knowledge on organic molecular systems achieved by using muons as well as expanding the RIKEN’s worldwide networks and linkages in collaborative research endeavors. Additionally, this activity also aims to encourage young students and researchers to work in the muon field in the future.

As an additional activity preceding the 4th ICFMS 2018, the organizing committee also offered a paper writing clinics for participants, especially for young scientists and students.

We believed great participation from all participants, organizing committees, and all reviewers made our conference successful.

Editor

Risdiana

Darminto

Budhy Kurniawan

A.A. Nugroho

Isao Watanabe

Organizer ICFMS 2018

Advisory Board

Prof. Yoji Koike (Tohoku Univ-Japan)

Dr. Isao Watanabe (RIKEN-Japan)

Prof. Shukri Sulaiman (University Sains Malaysia)

Prof. Andrivo Rusydi (National University of Singapore)

Dr. A. Agung Nugroho (Institut Teknologi Bandung)

Prof. Suminar Pratapa (Institut Teknologi Sepuluh Nopember)

Dr. Kuwat Triyana (Universitas Gadjah Mada)

Dr. Budhi Kurniawan (Universitas Indonesia)

Chairman

Prof. Darminto (Institut Teknologi Sepuluh Nopember)

Co-Chairman

Prof. Risdiana (Universitas Padjadjaran)

Secretary

Dr. Malik Anjelh Baqiya (Institut Teknologi Sepuluh Nopember)

Treasure

Dr. Lusi Safriani (Universitas Padjadjaran)

Organizing Committee

Dr. Togar Saragi (Universitas Padjadjaran)

Dr. Ayi Bahtiar (Universitas Padjadjaran)

Dr. Mochamad Zainuri (Institut Teknologi Sepuluh Nopember)

Dr. Yoyok Cahyono (Institut Teknologi Sepuluh Nopember)

Dr. Zaenal Arifin (Institut Teknologi Sepuluh Nopember)

CO. Website Builders: Ali Mufid, M.Si (Institut Teknologi Sepuluh Nopember)

Table of Contents

Preface

Chapter 1: Advanced and Functional Materials

The Study on Tuning Photoluminescence of Colloidal Graphene Quantum Dots Synthesized through Laser Ablation F.H. Murdaka, A.A. Nugroho, A. Kusumaatmaja, Isnaeni and I. Santoso	3
Crystal Structure and Electrical Properties of (1-x) (Ba_{0.85}Sr_{0.15})TiO₃ - x(K_{0.5}Na_{0.5})NbO₃ System U. Nuraini, Y.N. Kaukaba, Mashuri and Suasmoro	8
Precipitated Silica from Sodium Silicate by CO₂ on Fixed Bed Column R. Dewati, Suprihatin, K. Sumada and S. Muljani	14
The Morphology of Si-K-HAs Composite Prepared by Spray Drying S. Muljani, H. Setyawan and K. Sumada	19
Mechanical Exfoliation of Reduced Graphene Oxide From Old Coconut Shell as Radar Absorber in X-Band A.F. Kurniawan, M.S. Anwar, K. Nadiyyah, Mashuri, Triwikantoro and Darminto	25
Characterization of TiN Oxide Doping Antimony Thin Layer with Sol- Gel Spin Coating Method for Electronic Device A. Doyan, Susilawati, A. Harjono, S. Azzahra and M. Taufik	30
The Effects of Layer Thickness of Radar Absorbing Materials Prepared by Double Layer Method on X-Band Wavelength Frequency M. Zainuri, R.F. Puspitasari, D. Ristiani and Triwikantoro	35
Geopolymer Concrete for Radiation Shielding Application Nurhasmi, D. Tahir, B. Abdullah, A. Ansar, S. Ilyas, I. Mutmainna and W.I. Madda	41
Effects of Spin-Orbit Coupling on the Electronic and Excitonic Structures of Monolayer WS₂ B.E. Dharma, A. Syahroni and M.A. Majidi	48
Characterization of BaM and PaNi-Based Radar Absorbency (RAM) Behavior with Multilayer Geometry Structure for X-Band Absorption M. Zainuri and D. Andryani	54
Preparation and Characterization of Electrospun Composite Fiber of Polymer-TiO₂ G. Yudoyono, Sudarsono and D. Anggoro	60
Structural Analysis and Electrical Properties of Amorphous Carbon Thin Films D.I. Pamungkas, Mukarromah, B. Priyanto, H. Nakajima, S. Tunmee and Darminto	66
Optical Transmission of p-Type a-Si:H Thin Film Deposited by PECVD on ITO-Coated Glass S. Prayogi, M.A. Baqiya, Y. Cahyono and Darminto	72
Synthesis of Silica-Potassium-Nitrogen from Carbamide and Potassium Silicate by CO₂ Precipitator K. Sumada, S. Muljani and C. Pujiastuti	77
Effect of Modified SiO₂ on the Hydrophobic Properties as Self-Cleaning Materials L. Silvia, A.H. Wardani, Y. Dwihapsari and M. Zainuri	83
Particle Size Analysis of the Synthesised ZrO₂ from Natural Zircon Sand with Variation of pH Deposition Using Alkali Fusion-Coprecipitation Method C.F.K. Murti, H. Aldila, Endarko and Triwikantoro	89
Fabrication of Amorphous Carbon Thin Film from CH₄ Using PEVCD B. Priyanto, M. Saleh, S. Tunmee, C. Euaruksakul, Y. Cahyono, Triwikantoro and Darminto	95
Low Temperature Graphene Growth Effort on Corning Glass Substrate by Using VHF-IP HWC-PECVD M.A. Yusuf, A. Rosikhin, J.D. Malago, F.A. Noor and T. Winata	100
Electrochemical Deposition of Polyaniline on Carbon Steel for Corrosion Study in Geothermal Solution G.A. Aristia, L.Q. Hoa and R. Baessler	107

Chapter 2: Bio- and Food Technologies, Materials in Biomedicine

Relationship between the Structure and Electrical Conductivity of 12-Mer Single-Stranded Polyadenine Studied by Scanning Tunnelling Microscope H. Rozak, W.N. Zaharim, I. Miyazaki, N.E. Ismail, S.N. Abu Bakar, D. Kernain, R. Samian, K. Ichimura, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe	119
Study of Carbonated Calcium Phosphate Precipitation on Collagen R. Tasomara, S. Julia, Y.W. Sari, Nurlily and D.S. Soejoko	126
Physicochemical and Cytotoxicity Characterization of Injectable Bone Substitute Based on Hydroxyapatite - Chitosan - Streptomycin for Spinal Tuberculosis Cases S.A. Rachmawati, D. Hikmawati, A.S. Budiadin and A.P. Putra	133
Quality Improvement of Biomaterial of <i>Lemna</i> Sp Y. Andriani, Iskandar, I. Zidni and Risdiana	139
Hydroxyapatite-Collagen Composite Made from Coral and Chicken Claws for Bone Implant Application Siswanto, D. Hikmawati, Aminatun and M. Zamawi Ichsan	145
Study on Formalization of Oil Palm Trunk Modified by Melamine Formaldehyde T.N. Manik, Mashuri and Darminto	151
The Role of Relative Humidity on Physical Characteristics of Poly Vinyl Alcohol-<i>Aloe vera</i> Fiber Membrane by Using Electrospinning Methods D. Hikmawati, E.F. Adiputri, A.P. Putra and J. Ady	157
Synthesis of Carbon Nanosphere at Low Temperatures Based on Bamboo Fiber Y.K. Lahsmin, D. Tahir, B. Abdullah, S. Ilyas and I. Mutmainna	163
Irradiation Effect on the Structural Properties of <i>Ipomoea batatas</i> L as a Function of Temperature and Time S. Fatimah, M. Nur, S.D.A. Ilyas and D. Tahir	169
Sorption Efficiency in Dye Removal and Thermal Stability of Sorghum Stem Aerogel E.L. Septiani, O.P. Prastuti, Y. Kurniati, M. Fauziyah, Widiyastuti, H. Setyawan, Wahyudiono, H. Kanda and M. Goto	175
Investigation of Structural and Antifungal Behaviors of Nano-Sized Anatase Titanium Dioxide Synthesized by Co-Precipitation Route A. Taufiq, D. Arista, Sunaryono, R.E. Saputro, N. Hidayat, S. Soontaranon, E. Handoko and Darminto	181
Optimization of Polydimethylsiloxane Synthesized Parameters as Vitreous Humour Substitutes S. Setiadji, Fitrilawati, A.N. Fauza, A. Ardi, R.M. Novianti, N. Syakir, Waslaluiddin, I. Rahayu, A.S. Kartasasmita and Risdiana	189
Physical Characteristics of Soft Tissue Phantom from Silicone Rubber Based Vulcanization System A. Ansar, D. Tahir, B. Abdullah, Nurhasmi, S. Fatimah and Jusmawang	194
Synthesis of Precipitate Calcium Carbonate with Variation Morphology from Limestone by Using Solution Mixing Method Z. Arifin, Triwikantoro, B.A. Subagyo, M. Zainuri and Darminto	200
Banana Peel Activated Carbon in Removal of Dyes and Metals Ion in Textile Industrial Waste O.P. Prastuti, E.L. Septiani, Y. Kurniati, Widiyastuti and H. Setyawan	204
The Analysis of Composite Particle Board Based on Mushroom Growing Media Waste T.P. Harmi, Sutarman, W. Edi, A. Faldy, A. Syamsul and G.A.N. Fitri	210
Solvent Effect on Bond Dissociation Enthalpy (BDE) of Tetrahydrocurcumin: A Theoretical Study L.S.P. Boli, N.D. Aisyah, V. Khoirunisa, H. Rachmawati, H.K. Dipojono and F. Rusydi	215
The Effects of Split Valence Basis Sets on Muon Hyperfine Interaction in Guanine Nucleobase and Nucleotide Structures W.N. Zaharim, S. Sulaiman, S.N. Abu Bakar, N.E. Ismail, H. Rozak and I. Watanabe	222
Predicting Notable Radical Scavenging Sites of Gnetin C Using Density Functional Theory V. Khoirunisa, L.S.P. Boli, R. Nur Fadilla, A.G. Saputro, H. Rachmawati, H.K. Dipojono and F. Rusydi	229

Chapter 3: Investigation of Magnetic and Superconducting Properties

Synthesis and Characterization of Magnetic Rubidium Superoxide, RbO₂ F. Astuti, M. Miyajima, T. Fukuda, M. Kodani, T. Nakano, T. Kambe and I. Watanabe	237
Electrical Transport Properties of Perovskite La_{0.7}Sr_{0.2}Ba_{0.1}Mn_{1-x}Ni_xO₃ (x = 0 and 0.1) Manganite D.R. Munazat, B. Kurniawan and A. Imaduddin	243
The Doping Effects of SiC and Carbon Nanotubes on the Manufacture of Superconducting Monofilament MgB₂ Wires A. Imaduddin, Samsulludin, M.R. Wicaksono, I. Saefuloh, S. Herbirowo, S.D. Yudanto, Hendrik, H. Nugraha, Lusiana, E. Mabruri, N. Darsono and A.W. Pramono	249
Magnetic Properties of YBa₂Cu₃O₆ Studied by Density Functional Theory Calculations I. Ramli, S.S. Mohd-Tajudin, M.R. Ramadhan, D.P. Sari, S. Sulaiman, M.I. Mohamed-Ibrahim, B. Kurniawan and I. Watanabe	257
Enhanced Room-Temperature Ferromagnetism in Superconducting Pr_{2-x}Ce_xCuO₄ Nanoparticles M.A. Baqiya, P.E.D. Putra, R. Irfanita, Suasmoro, Darminto, T. Kawamata, T. Noji, H. Sato, M. Kato and Y. Koike	263
Magnetic Properties of Hole-Doped Pyrochlore Iridate (Y_{1-x-y}Cu_xCa_y)₂Ir₂O₇ J. Angel, R. Asih, H. Nomura, T. Taniguchi, K. Matsuhira, M.R. Ramadhan, I. Ramli, M. Wakeshima, Y. Hinatsu, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe	269
Physical Properties of Encapsulated Iron Oxide T. Saragi, B. Permana, A. Therigan, S. Hidayat, N. Syakir and Risdiana	277
Characterization of Barium M-Hexaferrite with Doping Zn and Mn for Microwaves Absorbent Susilawati, A. Doyan, M. Taufik, Wahyudi, E.R. Gunawan, A. Fitriani and Nazarudin	282
Comparative Study on Magnetism of Reduced Graphene Oxide (rGO) Prepared from Coconut Shells and the Commercial Product R. Asih, E.B. Yutomo, D. Ristiani, M.A. Baqiya, T. Kawamata, M. Kato, I. Watanabe, Y. Koike and Darminto	290
Magnetic Study of the Lower Critical Field of Organic Superconductor λ-(BETS)₂GaCl₄ D.P. Sari, K. Hiraki, T. Nakano, M. Hagiwara, Y. Nozue, T. Kusakawa, A. Hori, A. Yamamoto, I. Watanabe and Y. Ishii	296
Complex Permittivity, Permeability and Microwave Absorption Studies of Double Layer Magnetic Absorbers Based on BaFe₁₂O₁₉ and BaFe₁₀CoZnO₁₉ E. Handoko, I. Sugihartono, M.A. Marpaung, U. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono, M. Randa and M. Alaydrus	302
Preparation of Local Raw Material for α-Fe₂O₃ Nanoparticles Powder from Mineral Extraction of Iron Sand M.P. Izaak, H. Sitompul, W.A. Adi and Y.E. Gunanto	308
Study of Magnetic Properties in Electron Doped Superconductor Eu_{2-x}Ce_xCuO_{4+α} Y. Maryati, N. Nafisah, D.G. Auliya, E. Nurwati, T. Amalia, Y.R. Tayubi, T. Saragi and Risdiana	314
Crystal Structure and Magnetic Properties of Non-Stoichiometric Co₂MnGa Heusler Alloy M.Y. Pandu Akbar, R.R. Sihombing, A. Sakai, A.A. Nugroho and S. Nakatsuji	319
Analysis of Physical Properties, Crystal Structure and Magnetic Properties of Barium Hexaferrite Doped with 2 % wt. of SrO and Prepared by Coprecipitation Method Suprapedi, Muljadi, Djuhana and Ramlan	325
Effect of Copper Substitution on the Electrical Transport Properties of La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{1-x}Cu_xO₃ (X = 0 and 0.05) Manganites B. Kurniawan, D.S. Razaq and A. Imaduddin	331
Enhanced Microwave Absorbing Capabilities of Multilayer Absorbers Based on BaFe₁₂O₁₉ and Fe₃O₄ E. Handoko, I. Sugihartono, M.A. Marpaung, U. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono and M. Alaydrus	338
The Effect of Freezing-Thawing Route Number on Magnetic Properties and Nanostructural of Fe₃O₄/ Carboxymethyl Cellulose/Polyvinyl Alcohol Magnetic Hydrogel Sunaryono, M.N. Kholifah, A. Taufiq and E. Handoko	344

Synthesis and Characterization of Nd₂Fe₁₄B Powder Prepared by Using Milling and Heat Treatment	
Ramlan, P. Sardjono, Muljadi, D. Setiabudidaya and F. Gulo	352
Growth of Free-Standing La_{2-x}Sr_xCuO₄ Nanoparticles	
S. Winarsih, F. Budiman, H. Tanaka, T. Adachi, T. Goto, B. Soegijono, B. Kurniawan and I. Watanabe	357
Study of Magnetoresistance Effect and Magnetic Properties of La_{0.67}Sr_{0.33}Mn_{1-x}Ni_xO₃ (x = 0 and 0.2) Material Prepared by Sol-Gel Method	
U. Widyaiswari, B. Kurniawan, A. Imaduddin and I. Watanabe	363
 Chapter 4: Materials for Technologies of Energy Storage and Conversion	
Characteristics of Large Area Perovskite Solar Cells from Electrodes of Used Car Batteries	
A. Bahtiar, C. Agustin, E.S. Nurazizah, A. Aprilia and D. Hidayat	373
Study of Electrochemical Deposition Process of Graphene Oxide on DSSC TiO₂ Based Photoanode	
A. Aprilia, V. Marcelina, F. Yuliasari, Y.W. Hartati, FitriLawati, L. Safriani and R.E. Siregar	378
The Effect of Reduced Graphene Oxide (rGO) Coating on Electrical Conductivity of Lithium Ferro Phosphate (LFP) as an Alternative Cathode for Li-Ion Battery	
E. Suarso, A.Z. Laila, F.A. Setyawan, M. Zainuri, Z. Arifin and Darminto	386
Preparation of Lithium Iron Phosphate-Carbon Composite as a Cathode for Lithium Ion Battery	
I. Rahayu, A.R. Noviyanti, D. Rakhmawaty, A. Anggraeni, H.H. Bahti, S. Hidayat and Risdiana	392
Analysis of Defects and Surface Roughness on the Hydrogenated Amorphous Silicon (a-Si:H) Intrinsic Thin Film for Solar Cells	
Y. Cahyono, N. Dwi Purnamasari, M. Zainuri, S. Pratapa and Darminto	398
μSR Study with Light Irradiation of P3HT:ZnO Nanoparticles as Active Material of Hybrid Solar Cells	
L. Safriani, Risdiana, FitriLawati, A. Bahtiar, A. Aprilia, R.E. Siregar, M. Manawan, D. Puspitasari Sari, J. Angel and I. Watanabe	404
Band Gap Optimization of Thin Film a-Si:H Bifacial Solar Cells (BFSCs) Using AFORS-HET	
D. Hamdani, Y. Cahyono, G. Yudoyono and Darminto	409
Structure, Chemical Stability and Magnetic Properties of Lanthanum Silicate Oxide Apatite Synthesized by Hydrothermal Method	
Y.T. Malik, A.R. Noviyanti, N. Akbar, I. Hastiawan, T. Saragi and Risdiana	415
Effect of Electrical Resistance of TiO₂ Layer Characteristics of Dye Sensitized Solar Cell Using Chlorophyll as a Sensitizer	
N. Puspitasari, N.Y. Cahaya, G. Yudoyono, G. Prajitno and Darminto	422
Energy Storage Characteristics of Electrochemically Deposited Graphene Oxide on ITO and Cu Substrates	
FitriLawati, V. Marcelina, D.U. Dzujah, A. Bahtiar, Y.W. Hartati and N. Syakir	428
Characteristics of CMC from Corncob and its Application as Electrode Binder in Lithium Ion Battery	
S. Hidayat, I. Mubarak, B. Adiperdana, B.J. Suroto, N. Riveli, Y.W. Hartati and I. Rahayu	433
Synthesis of n-Doped Reduced Graphene Oxide from Coconut Shell as Supercapacitors	
I. Khambali, I.S. Ardiani, A.R. Kurniawan, Triwikantoro, M. Zainuri and Darminto	437
Synthesis and Characterization of Supercapacitor Electrode from Fiber of <i>Borassus flabellifer</i> L by Activation Method	
F.A. Prasetya, U. Anggarini, Y. Zakaria and R.D.S. Putri	444
Bi Doping Effect on the Conductivity of Lanthanum Silicate Apatite	
A.R. Noviyanti, N. Akbar, I. Hastiawan, I. Rahayu, Haryono, Y.T. Malik and Risdiana	451
Effect of Ni Doping Variations on Microstructure and Conductivity of Cathode LiNi_xFe_{1-x}PO₄/C Materials	
M. Zainuri, B.A. Anang and E. Novialent	456

Chapter 5: Modeling, Computational Procedures and Devices in Research of Functional Materials

Effects of the Supercell's Size on Muon Positions Calculations of La_2CuO_4 M.R. Ramadhan, I. Ramli, M.D. Umar, S. Winarsih, D.P. Sari, A. Manaf, B. Kurniawan, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe	465
Study on the Diffusion Rate of the Charge Carrier Transport in Regio-Random P3HT N. Riveli, B. Adiperdana, L. Safriani, B.J. Suroto, A.R. Noviyanti, I.H. Mohammad, I. Rahayu, M. Manawan, T. Saragi and Risdiana	471
An Approach to the Intermediate State of the Distributed Internal Fields on Muon Site M.D. Umar and I. Watanabe	476
μSR Spectrum Reconstruction Using Monte Carlo Approach: A Preliminary Study B. Adiperdana and Risdiana	483
Optical Spectra of Bi_2Se_3: The Effects of Electron-Hole Interactions D.N. Asturo, A. Syahroni and M.A. Majidi	489
Effects of Polarization Function on the Spin Contamination and Distribution in β'-$\text{Me}_4\text{P}[\text{Pd}(\text{dmit})_2]_2$ S.N.A. Ahmad, S. Sulaiman, L.S. Ang and I. Watanabe	494
Numerical Simulation on Effects of TCO Work Function on Performance of a-Si:H Solar Cells A. Sholih, D. Hamdani, S.T. Wicaksono, M.I.P. Hidayat, Y. Cahyono and Darminto	501
A Potential Application of Photonic Jet in Observing Micro-Metric Materials A. Abdurrochman, M.O. Wahidullah, D. Naufal, D.S. Sofiati, A. Aprilia, L. Safriani, S. Perrin and S. Lecler	507

Solvent Effect on Bond Dissociation Enthalpy (BDE) of Tetrahydrocurcumin: A Theoretical Study

Lusia Silfia Pulo Boli^{1,2,a}, Nufida Dwi Aisyah^{1,2,b}, Vera Khoirunisa^{1,3,c},
Heni Rachmawati^{4,5,d}, Hermawan Kresno Dipojono^{1,5,e},
and Febdian Rusydi^{2,6,*}

¹Department of Engineering Physics, Faculty of Industrial Engineering, Institute Teknologi Bandung, Bandung 40132, Indonesia

²Research Center for Quantum Engineering Design, Universitas Airlangga, Surabaya 60115, Indonesia

³Engineering Physics Study Program, Institut Teknologi Sumatera, Lampung 35365, Indonesia

⁴School of Pharmacy, Institut Teknologi Bandung, Bandung 40132, Indonesia

⁵Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Bandung 40132, Indonesia

⁶Department of Physics, Faculty of Science and Technology, Universitas Airlangga, Surabaya, 60115

^alusia_silfia@yahoo.co.id, ^bnufidadwiaisayah@gmail.com, ^ckhoirunisa.vera@gmail.com,
^dh_rachmawati@fa.itb.ac.id, ^edipojono@gmail.com, *rusydi@fst.unair.ac.id

Keywords: Bond Dissociation Enthalpy, Density Functional Theory, Solvent Effect.

Abstract. Solvent effect on bond dissociation enthalpy (BDE) of different functional groups of tetrahydrocurcumin is investigated. This is to evaluate how the polarity of a medium affect BDE and to clarify which functional groups hold the key role in its antioxidant activity through hydrogen transfer. We occupy density functional theory to calculate BDE through geometrical optimization and frequency calculation at six sites of tetrahydrocurcumin in water, methanol and chloroform solvents. The solvents represent polar and non-polar medium. Our result shows that BDE is lower in non-polar medium and hydrogen transfer is favored in this medium. A phenolic group is responsible for the antioxidant activity of tetrahydrocurcumin.

Introduction

Tetrahydrocurcumin ($C_{21}H_{24}O_6$), a polyphenol, is a derivative of curcumin that possesses antioxidant activity. This molecule is produced through hydrogenation of curcumin [1], which is extracted from the root of turmeric (*Curcuma longa*) [2]. In Indonesia, turmeric is commonly used as a spice. One latest research revealed that tetrahydrocurcumin has a significant protective effect against lipid peroxidation. This protective effect is due to the antioxidant activity of tetrahydrocurcumin [3].

Antioxidant activity of an antioxidant molecule, as well as tetrahydrocurcumin, is correlated to its ability to transfer a hydrogen atom toward free radical hence preventing it to promote lipid peroxidation [4]. Bond dissociation enthalpy (BDE) is one criterion to measure antioxidant activity. Low X-H BDE marks an easy dissociation, thus a fast hydrogen atom transfer from antioxidant molecule toward free radical can be achieved.

Evaluation of the antioxidant activity of tetrahydrocurcumin has a long history. In 1995, Osawa et.al evaluates antioxidant activity of curcuminoids and their derivatives by using linoleic acid and concludes that tetrahydrocurcumin has the highest protective effect [5]. By performing an assay using an organic radical in methanol solution, Portes et.al shows that tetrahydrocurcumin is more efficient in scavenging the organic radical as compared to curcumin. They attribute this efficiency to the presence of benzylic hydrogen in tetrahydrocurcumin [6]. Morales et.al agrees with their result but attribute

the efficiency to the presence of phenolic and enolic groups in tetrahydrocurcumin [1], see Fig 1. The disagreement on which functional groups of tetrahydrocurcumin holds the key role to its antioxidant activity has triggered us to evaluate BDE to clarify this problem.

We aim our research to evaluate the BDE of tetrahydrocurcumin in various solvents that represent polar and non-polar medium and to formulate how solvents affect the BDE by occupying density functional theory (DFT). In one previous study which uses DFT to evaluate BDE of resveratrol (a molecule with one phenolic group), it is concluded that BDE is lower in the gas phase and non-polar medium. Thus, we would expect that dissociation of an X-H bond of tetrahydrocurcumin is affected by the polarity of the medium [7]. Three solvents are chosen to represent polar and non-polar medium, which are water (we assume that biological system contains mostly water), methane (antioxidant assay is mostly done in methanol environment [6]), and chloroform. Water and Methanol represent a polar medium while chloroform represents a non-polar medium.

Computational Details

We conduct our research by using a DFT scheme. DFT solves Kohn-Sham equation numerically to generate electronic energy of many-electron system. To do so, two approximations which are exchange-correlation (XC) functionals and basis set (BS) are needed. In this research, tetrahydrocurcumin which consists of carbon, hydrogen and oxygen atoms is chosen as the many-electron system. We also choose M05-2X functional and 6-31++G(d,p) BS as our approximations for two reasons. First, the developer of M05-2X functional suggests it for bond dissociation energies calculation [8]. Second, 6-31++G(d,p) adds polarization and diffuse functions on hydrogen atoms.

All calculation is performed using a Gaussian 09 program package [9]. We do our calculation in two ways, (1) full geometry optimization and frequency calculation using M05-2X//6-31++G(d,p) directly, and (2) full geometry optimization and frequency calculation using M05-2X//6-31G then continue to single-point energy (SPE) and frequency calculations using M05-2X//6-31++G(d,p). Full geometry optimization predicts the most stable geometry of tetrahydrocurcumin as well as calculating its electronic energy. SPE calculation calculates the electronic energy of certain geometries. Meanwhile, frequency calculation will ensure that the calculated geometries are located at the lowest point of a potential well. We conduct our research in three stages as follow.

Stage 1: Geometry calculation at the ground state. First, we vary the orientation of -OH and -OCH₃ groups at the phenolic group of tetrahydrocurcumin in three different combinations. Then we calculate

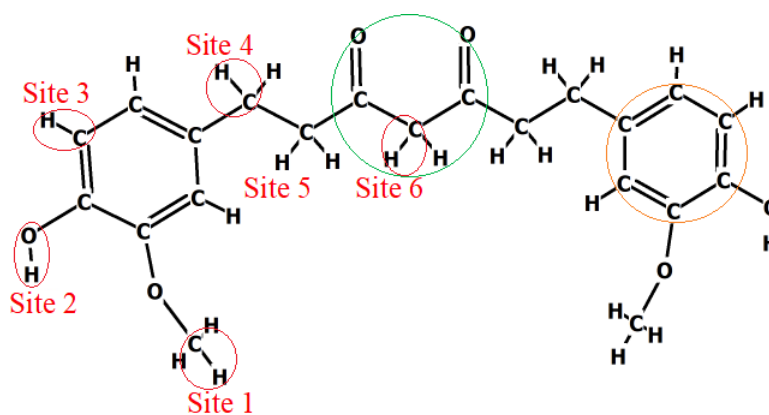


Fig. 1: Kekule structure of tetrahydrocurcumin. There are two information presents through this figure. (1) Functional groups of tetrahydrocurcumin which are marked by green and orange circles. The green circle marks beta-diketone group (this group can be arranged in either diketo or enol tautomer) and orange circle marks benzene group. When -OH group is included in the benzene group, it is called a phenolic group. (2) Six chosen sites of tetrahydrocurcumin marked by site 1 until site 6.

the electronic energy of each combination. The aim of this stage is to determine which combination is the molecular geometry of tetrahydrocurcumin at the ground state. The molecular geometry is used to verify that XC functional and BS chose are appropriate to study tetrahydrocurcumin system.

Stage 2: Tetrahydrocurcumin in solvents. Second, we continue to calculate the electronic energy of tetrahydrocurcumin and tetrahydrocurcumin radical in various solvents environment. The solvent effect is built with the polarized continuum model (PCM) method [10], where the solvent is modeled as a cavity with certain dielectric constant.

Tetrahydrocurcumin radical is formed when dissociation occurs, which is in this research is performed through one hydrogen atom abstraction from site 1 to 6 (see Fig 1). Site 1, site 2 and site 3 represent C-H and O-H bonds at a phenolic group. Site 4 and site 5 represent C-H bonds at the carbon chain. Meanwhile, site 6 represents C-H bond at the beta-diketone group. Abstraction sites are only chosen from one part of the molecule due to the symmetrical geometry of the tetrahydrocurcumin molecule. The radicals generated are called rad 1 to rad 6 based on the abstraction sites.

Stage 3: Bond Dissociation Enthalpy. Third, we calculate the BDE of tetrahydrocurcumin in three different solvents. Frequency calculation provides thermal correction to electronic energy yielding enthalpy (H) at 298.15 K. BDE of an O-H or C-H bond in tetrahydrocurcumin can be calculated according to Eq. 1. $H(\text{THC-H})$, $H(\text{THC}\cdot)$ and $H(\text{H}\cdot)$ represent enthalpy of tetrahydrocurcumin molecule that possesses complete hydrogen atoms, enthalpy of tetrahydrocurcumin molecule without one hydrogen atom (or also called tetrahydrocurcumin radical), and enthalpy of a hydrogen atom.

$$\text{BDE} = H(\text{THC}\cdot) + H(\text{H}\cdot) - H(\text{THC} - \text{H}) \quad (1)$$

Results and Discussion

Molecular Geometry of Tetrahydrocurcumin at the Ground State. Figure 2 displays optimized molecular geometry of tetrahydrocurcumin with three different combinations of -OH and -OCH₃ groups orientation. Among the combinations, the electronic energy of geometry (a) is 0.31 eV and 0.40 eV lower than electronic energy of geometry (b) and (c), respectively. From frequency calculation, we confirm that geometry (a) is located at the lowest point of potential well since there is no imaginary frequency is generated. In this geometry, the orientation of -OH group bends toward -OCH₃ group. This formation supports hydrogen bonding to form between H4 and O5 atoms, thus stabilizes this geometry. From this result, we suggest that geometry (a) represents the molecular geometry of tetrahydrocurcumin at the ground state.

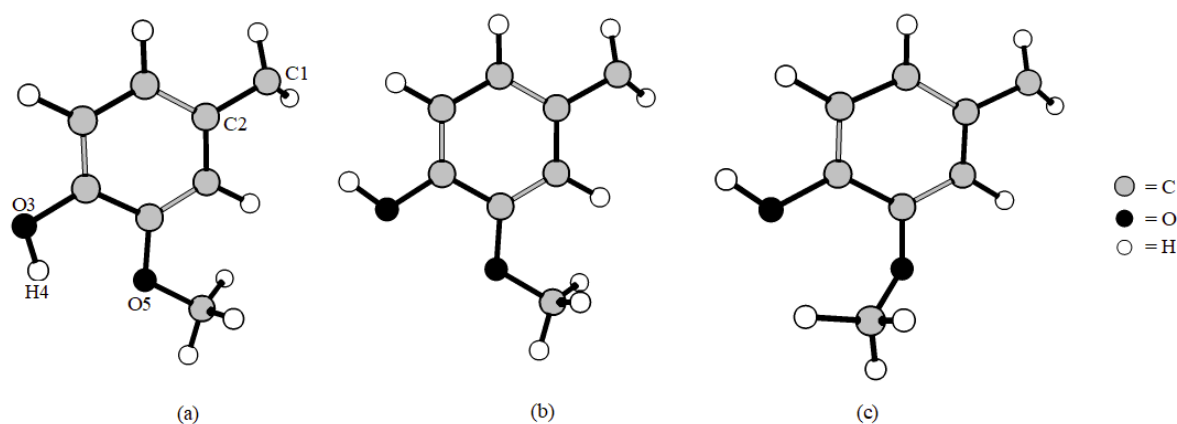


Fig. 2: Geometry (a), (b) and (c) present three different combinations of -OH and -OCH₃ groups at a phenolic group to form molecular geometry of tetrahydrocurcumin. Only one phenolic group of the molecule is presented to emphasize the combinations made. The atomic numbering in geometry (a) is presented to briefly explain this molecular structure according to Table 1.

Table 1 presents some calculated and experimental parameters of molecular geometry of tetrahydrocurcumin at the ground state. The atomic numbering used here is referring to Fig 2. We compare our calculated parameters to two previous experimental parameters, which are crystal structure of tetrahydrocurcumin [2] and phenol molecule at gas phase [11]. The difference between the calculated and experimental values of H4 and O5 distance is rather big. However, this distance is still in the range where a hydrogen bonding could form [2]. For C-C and O-H bonds, XC and BS chosen has managed to predict their bond length almost accurately. This verified that M05-2X and 6-31++G(d,p) are appropriate to study tetrahydrocurcumin molecule.

Table 1: Selected parameter of molecular geometry of tetrahydrocurcumin

Parameter ()	Calculated	Experiment	Δ
C1-C2	1.51	1.52 ^a	0.01
O3-H4	0.98	0.82 ^a , 0.96 ^b	0.02
H4 ··· O5	2.10	2.23 ^a	0.13

^a is taken from [2]

^b is taken from [11]

Tetrahydrocurcumin in solvents. Three different solvents, represent polar and non-polar medium, are selected in this research. They are water, methanol, and chloroform. In our simulation, the solvents are treated as a cavity with different dielectric constant. For the polar medium, which is water and methanol, the dielectric constants are 78.36 and 32.61. Meanwhile, for a non-polar medium, which is chloroform, the dielectric constant is 4.71.

Tetrahydrocurcumin can maintain its geometry as placed in a different solvents environment. In water and methanol solvents, C-C, O-H, and H···O values do not change (The values are 1.51, 0.97, and 2.10 Å, respectively). In chloroform solvent, the bond length of O-H increases by 0.01 Å. This slight elongation certainly will affect hydrogen bonding [12] that formed between H4 and O5 atoms.

As a good antioxidant candidate, tetrahydrocurcumin is expected to be very unreactive after transferring a hydrogen atom toward free radical. The unreactivity should be achieved to prevent the tetrahydrocurcumin radical re-abstracting a hydrogen atom from free radical [4]. One way to measure this unreactivity is from its electronic energy.

The relative electronic energy of tetrahydrocurcumin radicals in water, methanol and chloroform solvents is reported in Table 2. In water and methanol solvents, the electronic energy is increasing in the following order : Rad 2 < Rad 4 < Rad 6 < Rad 5 < Rad 1 < Rad 3. Low electronic energy in Rad 2 can be explained from the largest reduction of bond length near the abstraction site as a compensation to the loss of hydrogen - the reduction is 0.12 Å. Compare to Rad 2, bond lengths near site 3 experience the least reduction among all - the reduction is only 0.01-0.02 Å. Thus, Rad 3 becomes the most unreactive. In chloroform solvent, the electronic energy of tetrahydrocurcumin radicals decreases by an average of 0.23 eV as compared to two previous solvents. The presence of this solvent stabilizes tetrahydrocurcumin radicals and greatly affects Rad 4, 5 and 6 by maintaining the changing of bond length near the abstraction sites in a moderate reduction - the reduction is in the average of 0.08 Å.

Bond Dissociation Enthalpy. As initial evaluation of tetrahydrocurcumin's antioxidant ability, it is necessary to consider BDE value. Low BDE value marks good antioxidant ability of tetrahydrocurcumin since it facilitates a hydrogen atom transfer toward free radical.

Table 3 reports the calculated BDE value of tetrahydrocurcumin in three different solvents. Site 2 has the lowest BDE value in all solvents studied, so it represents the first site that can transfer a hydrogen atom. This result has no conflict to previous results by Morales et.al [1] and Murakami et.al [13]. The use of XC functional that can treat non-covalent interaction like hydrogen bonding and BS that adds polarization and diffuse functions on hydrogen atoms in this research have lowered BDE value by 1.92 Kcal/mol as compared to the result reported by Murakami et.al. Beside Site 2, Site 4, 5 and

Table 2: Relative electronic energy of tetrahydrocurcumin radical at various solvents.

Rad	Water E[eV]	Methanol E[eV]	Chloroform E[eV]
Rad 1	0.71	0.70	0.49
Rad 2	0.00	0.00	0.00
Rad 3	1.40	1.39	1.20
Rad 4	0.33	0.33	0.13
Rad 5	0.41	0.41	0.08
Rad 6	0.35	0.35	0.16

Table 3: Calculated Bond Dissociation Enthalpy in Various Solvents at 298.15 K.

Abstraction Site (Bond)	BDE [kcal/mol]			
	Water	Methanol	Chloroform	Gas Phase
Site 1 (C-H)	97.42	97.42	95.61	86.28(88.20 ^c)
Site 2 (O-H)	81.82	82.31	80.95	
Site 3 (C-H)	114.04	114.07	112.60	
Site 4 (C-H)	87.77	87.79	86.16	
Site 5 (C-H)	90.34	90.35	86.81	
Site 6 (C-H)	89.74	89.81	88.49	

^c is taken from [13]

6, which are C-H bonds, should also be considered as a transfer site especially in chloroform solvent. The importance of C-H bonds of polyphenols in antioxidant activity has been stated previously by Hassanzadeh et.al [14]. We also observe a peculiar trend in Site 5 in the chloroform solvent. Table 2 reports that Rad 5 has lower electronic energy as compared to Rad 4. But increasing temperature to 298.15 K (when frequency calculation is performed) probably affects translation, rotation and vibrational motion of Rad 5 almost as much as Rad 4, thus contributes to their similar enthalpy values. Site 1 and 3 are the least to expect to involve in antioxidant activity of tetrahydrocurcumin. Dissociation at these C-H bonds in a phenolic group will promote the lowest electron delocalization in phenyl ring [15].

Conclusion

We have evaluated bond dissociation enthalpy of tetrahydrocurcumin in three different solvents represent polar and non-polar medium using density functional theory. Our results suggest that polarity of medium affects the BDE of tetrahydrocurcumin. Non-polar medium lowers BDE value, thus hydrogen transfer is favorable in this medium. Meanwhile, in a polar medium, hydrogen transfer is less favored. In our future work, we plan to check the antioxidant activity of tetrahydrocurcumin in a polar medium through electron transfer. Our calculation predicts O-H bond in a phenolic group that holds the key role to tetrahydrocurcumin antioxidant activity regardless of the medium. We also suggest C-H bond in the carbon chain as well as in beta-diketone group to be considered as hydrogen transfer sites.

Acknowledgement

We thank Institut Teknologi Bandung (ITB) and Research Center for Nanosciences and Nanotechnology (RCNN) for computer facilities support. We also thank "Hibah Mandat grant 2018 of Airlangga University" that has funded this research. Lusia thanks to Lembaga Pengelola Dana Pendidikan (LPDP) for the doctoral scholarship.

References

- [1] NP Morales, S Sirijaroonwong, P Yamanont, C Phisalaphong, Electron paramagnetic resonance study of the free radical scavenging capacity of curcumin and its demethoxy and hydrogenated derivatives, *Biol.Pharm.Bull.* 38 (2015)1478-1483
- [2] CR Giriya, NS Begum, AA Syed, V Thiruvengadam, Hydrogen-bonding and C-H \cdots π interactions in 1,7-bis(4-hydroxy-3-methoxyphenyl)heptane-3,5-dione (tetrahydrocurcumin), *Acta Cryst C60* (2004) o611-o613
- [3] P Chaniad, NP Morales, P Rojsitthisak, R Luechapudiporn, Effects of turmeric extract on hemin-induced low-density lipoprotein oxidation, *J Food Biochem* (2018)1-9
- [4] KU Ingold, DA Pratt, Advances in radical-trapping antioxidant chemistry in 21st century: A kinetics and mechanism perspective, *Chem. Rev.* 114(2014) 9022-9046
- [5] T Osawa, Y Sugiyama, M Inayoshi, S Kawakishi, Antioxidative activity of tetrahydrocurcuminoids, *Bioscience, Biotechnology, and Biochemistry* 59 (1995) 1609-1612
- [6] E Portes, C Gardrat, A Castellan, A comparative study on the antioxidant properties of tetrahydrocurcuminoids and curcuminoids, *Tetrahedron* 63 (2007) 9092-9099
- [7] A Benayahoum, H Amira-Guebailia, O Houache, Homolytic and heterolytic O-H bond cleavage in *trans*-resveratrol and some phenanthrene analogs: A theoretical study, *Computational and Theoretical Chemistry* 1037 (2014) 1-9
- [8] Y Zhao, NE Schultz, DG Truhlar, Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions, *J. Chem. Theory. Comput.* 2 (2006) 364-382
- [9] Gaussian 09, Revision D.01, 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, J. A. Montgomery, Jr., 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. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- [10] B Mennucci, J Tomasi, R Cammi, JR Cheeseman, MJ Frisch, FJ Devlin, S Gabriel, PJ Stephens, Polarizable continuum model (PCM) calculations of solvent effects on optical rotations of chiral molecules, *J. Phys. Chem. A* 106 (2002) 6102-6113

-
- [11] "Bond Lengths and Angles in Gas-Phase Molecules", in CRC Handbook of Chemistry and Physics, Internet Version 2005, David R. Lide, ed., <<http://www.hbcnetbase.com>>, CRC Press, Boca Raton, FL, 2005.
- [12] VP Gupta, 11-Topological Analysis of Electron Density - Quantum Theory of Atoms in Molecules, Principles and Applications of Quantum Chemistry 359-384
- [13] Y Murakami, H Ishii, N Takada, S Tanaka, M Machino, S Ito, S Fujisawa, Comparative anti-inflammatory activities of curcumin and tetrahydrocurcumin based on the phenolic O-H bond dissociation enthalpy, ionization potential and quantum chemical descriptor, Anticancer Research 28 (2008) 699-708.
- [14] K Hassanzadeh, K Akhtari, H Hassanzadeh, SA Zarei, N Fakhraei, K Hassanzadeh, The role of structural C-H compared with phenolic OH sites on the antioxidant activity of oleuropein and its derivatives as a great Non-flavonoid family of the olive components: a DFT study, Food Chemistry 164 (2014) 251-258.
- [15] KU Ingold, JS Wright, Understanding trends in C-H, N-H and O-H bond dissociation enthalpies, Journal of Chemical Education 77 (2000) 1062-1064.