UPRM-Chemical Engineering Graduate Research Symposium

Thursday, December 5th, 2013 – Stefani 113 & Sala Eugene Francis (Physics Building)

Sponsor:

P&G

Coordinator: Prof. Ubaldo M. Córdova-Figueroa

Agenda

Activity / Seminar Title	Speaker	Time
Breakfast (Sala Eugene Francis - Physics)		8:00-8:50AM
Welcome (at S 113)		8:50-9:00AM
Keynote: Superior Rigid and Flexible Nanoporous Materials for Adsorption Based Applications	Prof. Arturo Hernández	9:00-10:00AM
Break		10:00-10:15AM
The Effect of TiO_2 Nanoparticles on the Properties of Triblock Copolymer Membranes	Ariangelís Ortiz	10:15-10:45AM
Modelling of the fluid bed drying process	Vladimir Villanueva	10:45-11:15AM
Synthesis and Characterization of Polysiloxane-Based Magnetic Liquid Crystalline Elastomer Composite	Stephany Herrera	11:15-11:45AM
Lunch, Poster Session (at Sala Eugene Francis - Physics)		11:45AM-2:00PM
$Cu_2(pzdc)_2(bpy)$ Porous Coordination Pillared-Layer Networks: Long-Range Structural Changes Studied via In Situ High Pressure CO_2 Adsorption and X-ray Diffraction at Ambient Temperature	Karina Riascos	2:00-2:30PM
Effects of HSP70 inhibition in HeyA8 during Magnetic Fluid Hyperthermia Application	Karem Court	2:30-3:00PM
Electrical Characterization of Sulfonated Poly(Styrene-Isobutylene-Styrene) Triblock Copolymer Thin Films	Martha Rozo	3:00-3:30PM
Awards, Closing Remarks & Evaluation		3:30-4:00PM

Poster Presenters	**Title**
Camilo Mora	Characterization of the Molecular Response Toward β-Peptide in Fungi and Mammalian Cells
Kriziam Ortiz	Grafting Techniques for Blocking Micropores in Mesoporous Silica Adsorbents
Héctor Méndez	Synthesis and Characterization of a Novel Palladium Nanostructured Ensemble Supported in Anodized Alumina Membranes for Hydrogen Sensing Applications
Paul Meza	Computational Study of the Physical Adsorption of CO2 on Porous Coordination Polymers
Christian Rivera	Synthesis of Carbon Materials with improved Thermo Solvent Stability for Biomass-Derived dehydration Reactions
Vanesa Ayala	TBD
Glenn C. Vidal	Guided motion of self-propelled magnetic colloidal particles

Keynote Speaker: Prof. Arturo J. Hernández-Maldonado

Title: *Superior Rigid and Flexible Nanoporous Materials for Adsorption Based Applications*

Abstract:

This seminar will cover some of the most important challenges found in the design of adsorbent porous materials tailored for existing and emerging applications. Challenges include the incorporation of significant concentrations of metal sites that are readily accessible to adsorbates, tailoring of hydrophobicity, and development of flexible frameworks or structures with molecular gating capabilities while offering minimal impact on working adsorption capacities. Although the use of structure directing agents (SDAs) has brought many opportunities to the development of many novel topologies and porous matrix arrangements, it has also introduced problems related to the production of undesired secondary species. This seminar will include a discussion about the use of partial decomposition (detemplation) techniques as an attempt to simplify the post-synthesis functionalization of adsorption surfaces.

In terms of applications, this seminar will cover the use of adsorbent materials designed from the bottom-up for deep-removal of carbon dioxide from light gas mixtures and pharmaceutical and personal care products (emerging contaminants) from water, all at ambient conditions. The former application will focus on materials that rely on enhanced quadrupole moment/electric field interactions while the latter will focus on transition metal complexation-based adsorbents.

ABSTRACT

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Electrical Characterization of Sulfonated Poly(Styrene-Isobutylene-Styrene) Triblock Copolymer Thin Films

Martha Rozo Medina and *Agnes M. Padovani*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT:

Polymers are a fundamental part of electronic systems and are widely used due to their low cost, ease of processing, and their wide range of mechanical and electrical properties. They are traditionally used as passive components such as insulators and coatings, but more recent applications also include sensors, batteries, and low-temperature fuel cells. A thorough understanding of the electrical properties is necessary in order to improve their performance and to determine the best design conditions in any given application. The electrical properties of polymeric materials can be characterized through dielectric constant and loss tangent measurements. This work focuses on the electrical characterization of sulfonated poly (styrene-isobutylene-styrene) (SIBS) triblock copolymer thin films. More specifically, the dielectric properties of the SIBS thin films will be evaluated as a function of a variety of processing parameters such as the sulfonation percent. For the electrical studies, metal-insulator-metal (MIM) parallel-plate capacitors are fabricated using a combination of metal deposition, photolithography techniques, and spin-coating for the polymer films. The electrical measurements will be performed using a Network Analyzer that gives values of complex impedance over frequencies in the range of 100 kHz to 1 MHz. The values for the dielectric constant and dissipation factor can be derived from this data.

Keywords: SIBS thin films, dielectric constant, loss tangent, sulfonation percent, metal deposition, spin coating, photolithography.

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Modelling of the fluid bed drying process

Vladimir Villanueva López, Carlos Velázquez Figueroa
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ABSTRACT:

The drying of solids is one of the most common unit operation used in several industries, such as agrochemicals, foods, ceramic, pharmaceutical, mineral, polymer, textile, etc. The content of moisture is a crucial parameter especially in the pharmaceutical industry, for instance, the excess of water may considerably affect the stability of the Active Pharmaceutical Ingredient (API) and the efficiency of each stage in the process of solid dosage manufacturing. On the other hand, over drying causes high consumption of energy and possible degradation of the pharmaceutical materials. Those drawbacks represent economical losses for the companies that are offset by the increase on the prices of drugs. In order to address this need, a reliable mathematical model that can describe the mechanisms of heat and mass transfer in particulate systems coupled with an adequate implementation of control strategy will assure the quality of the products.

In this study, a realistic two phase mathematical model of the drying of particulate material found on the literature was programmed in an advanced process modelling software (gPROMS®). The model was validated predicting the moisture content and the temperature of a pharmaceutical formulation inside a fluid bed dryer.

Keywords: fluid bed dryer, two phase model, gPROMS®

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Characterization of the Molecular Response Toward β-Peptide in Fungi and Mammalian Cells

C. Mora-navarro[2], J. Caraballo[2], F. Chaparro[2], J. Nieves[1], B. Ortiz[2], S. Gellman[3], S. Palecek[4], M. Ryuls-Lee[4],
M. Torres-Lugo[2], P. Ortiz-Bermudez[2].
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University of Puerto-Mayaguez, Mayaguez, Puerto Rico
[3]Department of Chemistry, [4]Department of Chemical Engineering, University of Wisconsin-Madison, Madison, Wisconsin

The development of new drugs to treat fungal infections has become an urgent necessity due to the increasing resistant strains of fungi and bacteria, the currently limited selection of treatment and its adverse side effectsalong with the increasing numbers of immunocompromised patients. The β-peptides emerge as a possible solution since these are foldamers, like short nanorods, made from artificial amino acids, designed to mimic natural antimicrobial peptides known as host-defense peptides (HDPs). HDPs are made by most living forms as a way to counteract a broad spectrum of microbial attacks, which include bacteria and fungi. Someadvantages of using β-peptides compared to natural HDPs are: their conformational stability, predictable folding behavior, resistance to proteases and activity at physiological salt concentrations. From previous studies, the selected β-peptide sequence was β-(ACHC-V-K)$_3$ (nicknamed V2), because of its antifungal properties and low toxicity against erythrocytes; V2 was synthesized using a solid phase reaction like its synthetic α-peptide counterparts. The mechanism of action of β-peptides still remains unknown and in order tofind possible routes of action we hypothesized that, using a genetic molecular approach, we can identify genes that are actively involved in the phenotypic response of a genetic model and for this we used *S. cerevisiae*.Using this approach, 15 genes have been identified and these are currently being validated. V2 was tested ontwo different mammalian cell lines, HepG2 and Caco-2, and the IC50 was determined for an exposure time of 1 hour.

Keywords: beta-peptide , *Host-Defense Peptide, HDPs A*ntifungal drugs

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Guided motion of self-propelled magnetic colloidal particle

Glenn C. Vidal-Urquiza and *Ubaldo M. Córdova-Figueroa*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Self-propulsion of artificial micro/nano-scale objects in environment dominated by viscous forces and Brownian motion has aroused considerable interest nowadays. Diverse studies have been carried out in order to develop optimal design for propulsion, so that it can be used at its highest performance in potential applications of emerging novel technologies. However, it has been shown in recent experiments that the self-propulsion velocity is hindered by their rotary Brownian motion, and thus preventing its potential to be fully realized. This rotary diffusion induces a lost in its directional self-propulsion, reducing its ability to move effectively. The fashion to overcome this effect could be achieved with colloidal particles sensitive to external magnetic fields. Therefore, the present work proposes a simple model to study the spatiotemporal behavior of a self-propelled "active" colloidal particle that takes into account rotary Brownian motion and orientational control using a magnetic field. To this end, a theory was developed to determine the mean particle velocity and long-time self-diffusivity. In addition, an alternative solution using Brownian dynamics (BD) simulation is obtained and compared to the theory.

Keywords: active particles, magnetic field, self-diffusion, motion control

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Grafting Techniques for Blocking Micropores in Mesoporous Silica Adsorbents

Krisiam Ortiz-Martínez, *and Arturo J. Hernández-Maldonado*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

Ordered mesoporous silica materials such as SBA-15 have attracted great interest due to their high surface area, large pore size and a large number of silanol groups on their surfaces. These structural versatilities allow these materials to be used in many applications such as catalysis and adsorption. However, these mesoporous materials have poor stability in water due to the presence of micropores on their surfaces. These micropores promote the dissolution of the structural framework of these mesoporous materials. This is the result of the hydrolysis of the siloxane bonds, thus hindering the good performance of these materials in aqueous media applications. Due to this limitation, numerous efforts have been carried out to reduce these micropores in order to improve the performance of these materials. A few of these efforts include changing the synthesis conditions and adding inorganic salts during the post-synthesis. The present aim is to demonstrate the functionalization of SBA-15 materials, by successfully blocking micropores with amino-organics and transition metals using grafting techniques. Optimizing this post-synthesis modification of these mesoporous SBA-15 silica materials, will aid in the further development of adsorbent materials for use in aqueous media applications.

Keywords: SBA-15, hydrostability, micropores, transition metal grafting

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Title

Vanessa Ayala Rivera, *Madeline Torres-Lugo and Carlos Rinaldi*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Commonly, nanoparticles used in biomedical applications such as magnetic fluid hyperthermia (MFH), require a coating to prevent the agglomeration or aggregation of the particles. For this, various types of polymers and surfactants are used, being dextran and carboxymethyl dextran of frequent use. Studies related to particle stability with dextran coatings have been performed but in all those cases only one type of dextran was used, and the effect of molecular weight was not assessed nor its effects on nanoparticle-cell interactions. It is the aim of the present work to study the effect of magnetite nanoparticle composition on the nanoparticles' colloidal stability, its effects on the nanoparticle uptake by cancer cells, as well as its effects on *in vitro* and *in vivo* MFH. For this we prepared carboxy-methyl substituted dextrans of various molecular weights and reacted them using carbodiimide chemistry with amine-silane coated iron oxide nanoparticles. Colloidal stability of of carboxy-methyl substituted dextran coated nanoparticles was evaluated by Dynamic Light Scattering and Zeta Potential. Particles coated with the various molecular weights showed to be stable against precipitation and agglomeration in water and biological media. Cytotoxicity of these particles on breast cancer cells MCF-7 and ovarian cancer cells A2780 was evaluated. Particles seem to be non-toxic on the range of concentrations analyzed.

Keywords: Iron oxide, carboxymethyl dextran, molecular weight, nanoparticles, MFH

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Synthesis and Characterization of a Novel Palladium Nanostructured Ensemble Supported in Anodized Alumina Membranes for Hydrogen Sensing Applications

Héctor Méndez-Colberg, and *María Martínez-Iñesta*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: **A Pd/Anodic alumina membrane (AAM) ensemble was formed by using Solid State Reduction. The ensemble consisted of Pd thin films on both sides of the AAM with connecting nanowires as evidenced with Scanning Electron Microscopy images. Samples with 1.5%wt, 2.5%wt, 5%wt and 10% wt Pd were studied for applications in hydrogen sensing. X-ray diffraction was used to determine the concentration at which the alpha to beta Pd phase transition occurred. All samples responded to hydrogen but the sample with 2.5% wt Pd was the most sensitive and had the most accurate results with minimal baseline drifting. Results show that solid-state reduction is a facile and economical alternative for making Pd sensor elements.**

Keywords: Palladium, hydrogen sensor, Sensitivity, Response Time, Oxygen, Electrical Current

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Computational Study of the Physical Adsorption of CO_2 on Porous Coordination Polymers

Paul de Jesus Meza-Morales, *and María C. Curet-Arana*
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Coordination polymer-ligands (CPLs) are porous-crystalline materials consisting of metal ions linked to organic bridging ligands. Because of the flexibility in their synthesis, a range of novel structures has been rationally designed with high surface area, large pores and distinct gas adsorption properties. The objective of this project is to study CO_2 - CPLs (CPL-2, CPL-4, & CPL-7) interactions using quantum mechanical (QM) calculations. We have used representative models for the CPLs pores to reproduce binding sites in order to quantify energies of adsorption and characterize the nature of the interaction. For the QM calculations, we have compared two exchange/correlation functionals B3LYP and wB97XD, which has a specific treatment for non-covalent interactions. We have used a mix of 6-311+G and LANL2DZ for the basis sets. The latter basis set was used solely on the transition metal atom. In addition, charges from electrostatic potential using a grid based method (CHelpG), natural bond orbitals population analysis and electric field gradient calculations were performed to describe the partial atomic charge distribution and electric field properties of the framework. Our results demonstrate that:

- In the three CPL-n models, the dicarboxylate groups at *pzdc* have the greatest electric field gradient, which would be a potential interacting site for the CO_2 molecule.
- The average interaction energy for CPL-2, CPL-4 and CPL-7 were -30.54, -35.42 and -53.87 kJ/mol, respectively.
- The average interaction distance between CO_2 and the closest atom of the CPL-n models was around 2.7 Å in all the systems studied.
- In most cases, the electron density for CO_2 molecule interacting with CPL-n models increase compared to the isolated CO_2 molecule, however the CO_2 maintains its linearity in all the results.

Keywords: Porous Coordination Polymers (PCPs), Coordination Polymers Ligand (CPLs), CO_2 Sequestration, Density Functional Theory (DFT).

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Synthesis and Characterization of Polysiloxane-Based Magnetic Liquid Crystalline Elastomer Composite

Stephany Herrera-Posada[1], *Barbara Calcagno*[2] *and Aldo Acevedo*[1]
1 Department of Chemical Engineering, University of Puerto Rico-Mayagüez
2 Department of General Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Liquid crystalline elastomers (LCE´s) are liquid crystal polymers that combine the mechanical properties of rubbers with the ordered structure and mobility of LC phases. They have unique optical, mechanical and piezoelectric properties, which can be modified in response to external stimuli. The latter allows for potential applications such as mechanical actuators, in optics and sensing. In this work, we propose to improve the sensitivity of these elastomers to external stimuli by triggering mechanical and optical responses through external magnetic fields or viceversa. In order to do this, we are embedding into the LC elastomer chemically functionalized magnetic particles.

Polysiloxanes are ideal candidates due to their biocompatibility and known chemical synthesis and modification. The proposed liquid crystalline elastomer matrix consist of a polysiloxane backbone poly(methylhydrosiloxane), a mesogenic pendant group 4-methoxyphenyl-4(but-3-enyloxy)benzoate, and a bifunctional crosslinker 1,4-bis(undecyl-10-enyloxy)benzene. Preliminary results for the synthesis of LCEs composites based on this matrix and oleic acid functionalized iron oxide nanoparticles will be presented, as well as their thermal (DSC, differential scanning calorimetry), structural (POM, polarized optical microscopy) and mechanical (stress-strain behavior and Young's moduli) characterization. Results of their response to alternating magnetic fields will also be presented.

Keywords: liquid crystal elastomer, magnetic composites, polysiloxane

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The Effect of TiO_2 Nanoparticles on the Properties of Triblock Copolymer Membranes

Ariangelís Ortiz Negrón, David Suleiman
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Two block copolymers with different elastomeric blocks (poly (isobutylene) and poly (ethylene/butylene)) were sulfonated as a means to create a mechanism for proton transport. Titanium dioxide nanoparticles were added to the materials in order to improve thermal, mechanical and water absorption properties. These TiO_2 particles were functionalized to enhance their interactions with the polymers and to determine the effect of functionalizations on the studied properties. Materials were characterized by Fourier transform infrared spectroscopy, which confirmed the presence of the sulfonic groups and of the TiO_2 on the membranes and also confirmed the functionalization of the nanoparticles. The presence of new functionalities was also determined by thermogravimetric analysis. Thermogravimetric analyses were performed in order to determine the effect of the functionalization and the additives on the thermal stability of our materials. Titania particles had no effect on the degradation temperature of the polymer backbone while sulfonation increased by approximately 20 degrees the degradation temperature. Differences in stability were also observed for the different elastomers. Functional membranes need to be hydrated in order for them to transport protons. With water absorption experiments we confirmed that these materials absorbed up to five times their weight in water. Other characterizations performed on the membranes were regarding transport properties and ion exchange capacity (IEC). Methanol permeability results are similar to those of Nafion (the state of the art proton exchange membrane) for poly (styrene-ethylene/butylene-styrene) while for the poly (styrene-isobutylene-styrene) copolymer the permeation of the fuel is significantly higher. All membranes had high IECs and particles functionalization enhanced this property.

Keywords: block copolymers, nanocomposites, titanium dioxide, materials characterization

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Synthesis of Carbon Materials with improved Thermo Solvent Stability for Biomass-Derived dehydration Reactions

Rivera-Goyco, C.; Cardona-Martínez, N.
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT Fossil fuels provide approximately three quarters of today's fuel energy, but current fossil fuel world reserves will not meet future energy demands. Also, the burning of these energy sources, for energy purposes, is associated with an increase of CO_2 concentration in the atmosphere, and therefore are a cause for Global Warming. It is because of these problems that a transition from nonrenewable (fossil fuels) energy sources to a more environmental and renewable energy source is desirable. Biomass is the only renewable energy source which can substitute fossil fuels, but in order to achieve this some technical challenges must be solved. One technical challenge is the designing of catalysts with good thermo solvent stabilities. This is especially true for aqueous liquid phase processing, as for example dehydration reactions of biomass-derived feedstocks which are catalyzed by acids and bases. A possible solution, specifically for dehydration reactions of biomass- derived feedstocks, is the synthesis of carbon materials with high surface areas and acidic functionalities. So far, three different types of Mesoporous Carbon Materials have been synthetized by our group, which area CMK-3, CMK-5, and FDU-15. A phenyl sulfonic acid group has been attached to the surface of CMK-3. Characterization of the materials is being performed using Scanning Electron Microscope (SEM), Nitrogen Adsorption - Desorption Isotherms, and X-Ray Diffraction (XRD). Results to date indicate that the synthesized carbon materials have the desired ordered range of mesopores and textural properties. The functionalized CMK-3 lost its long range ordered mesopore structure. FDU-15 has also been synthesized but the synthesis procedure can still be improved.

Keywords: heterogeneous catalysis, dehydration of sugars, carbon materials, sulfonic acid

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Effects of HSP70 inhibition in HeyA8 during Magnetic Fluid Hyperthermia Application

Karem A. Court, Anil Sood, Carlos Rinaldi and Madeline Torres-Lugo.
Department of Chemical Engineering, University of Puerto Rico-Mayagüez

ABSTRACT: Ovarian cancer is one of the most common gynecological diseases. For 2013, the American Cancer Society reported an estimated of 22,240 new cases and 14,030 deaths. Hyperthermia has been used as cancer treatment. Hyperthermia is a type of cancer treatment where tissue is heated at temperatures between 41-47°C. In this research is used magnetic fluid hyperthermia (MFH). In MFH magnetic nanoparticles generate heat when they are exposed to a magnetic field. A gene expression study was performed in ovarian cancer HeyA8 cells line using MFH. Analysis revealed that heat shock protein genes including HSPA1A were overexpressed when treatment was applied at 43°C for 30 min. The expression of the gene was confirmed by PCR at 41 and 43°C.HSPA1A encodes the heat shock protein HSP70. The objective of this work is to determine the effects of HSP70 inhibition in HeyA8 during magnetic fluid hyperthermia application. The hypothesis states that the inhibition of HSP70 will decreases de cell viability when MFH is applied to cancer cells. 2-phenylethynesulfonamide (PES) was chosen to suppress HSP70 and would be use in combination treatment with magnetic fluid hyperthermia. It was observed a decreased in cell viability when the cells were exposed to MFH and PES drug. At 41°C and 30 minutes of exposure to MFH the cells do not suffer any damage. It was observed a decreased of 35% when cells were exposed to PES drug for 24 hours and 30 minutes treatment.

Keywords: Hyperthermia, HSP70, Ovarian Cancer, gene expression.

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$Cu_2(pzdc)_2(bpy)$ Porous Coordination Pillared-Layer Networks: Long-Range Structural Changes Studied via *In Situ* High Pressure CO_2 Adsorption and X-ray Diffraction at Ambient Temperature

Karina Riascos-Rodríguez,[a] *Aaron Schroeder,*[b] *Michael Arend,*[b]
Paul G. Evans[b] *and Arturo Hernández-Maldonado*[a]
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[b]Department of Materials Science and Engineering, University of Wisconsin-Madison

ABSTRACT: The arrangement of weak and strong motifs in metal organic frameworks (MOFs) favors the conformation of dynamic bridging which could also induce structural changes upon the presence of guest molecules such as CO_2. In this work, *in situ* high-pressure CO_2 adsorption and X-ray diffraction experiments performed at ambient temperature were used to estimate the long-range structural changes of a $Cu_2(pzdc)_2(bpy)$ (pzdc = pyrazine-2,3-dicarboxylate, bpy = 4,4 -bipyridine) (i.e., CPL-2) framework at different gas loadings. The changes in the main void volume of the structure, an apparent gallery for practical purposes, were estimated from changes observed in *d* spacing of key diffraction peaks or planes during CO_2 pressurization/depressurization cycles. An increase in gas pressure (stepwise up to 7 atm) resulted in a 2 Å^2 total increase in the cross-sectional area of a gallery. Upon desorption of CO_2, this area decreased only by 0.5 Å^2, indicating partial structural irreversibility. Similar changes were observed along *c*. These structural changes were plausibly related to cleavage and rotational freedom of the motifs present in the CPL-2 structure. For instance, Cu^{2+} nodes are able to experience changes in coordination mode while carboxylate groups could change their spatial conformation in the presence of electrostatic, attractive, repulsive, and physical fields. Studies of MOF distortion and structural changes produced during high-pressure gas uptake at ambient temperature are of utmost necessity to elucidate the stability of these materials for adsorption processes at the industrial scale.

Keywords: CO_2 adsorption, *in situ* high-pressure X-ray diffraction, CPL, metal organic frameworks.