ITI HiFunMat Master Internship Proposal

☒ M 1 ☐ M 2

Design, synthesis and characterization of luminescent host-guest inorganic-organic systems

Internship supervisor

Name, first name	ROGEZ Guillaume & D'ALEO Anthony
E-mail, Telephone	guillaume.rogez@ipcms.unistra.fr, anthony.daleo@ipcms.unistra.fr
Laboratory	Institut de physique et chimie des Matériaux de Strasbourg (IPCMS UMR 7504)
Collaboration with a HiFunMat member (*please indicate their name*)	☒ No ☐ Yes :

Student profile looked for

Master program (*more than one box can be ticked)*	☒ Material science and engineering ☒ Chemistry ☐ Physics
Other indications if necessary	

Internship description

Ion-exchangeable layered metal oxides have received growing attention because they can be functionalized under soft conditions, providing access to a very wide variety of kinetic metastable phases, inaccessible *via* classical solid-state reactions.[1–3] Such new phases, recently reviewed,[4] range from complex new inorganic solids,[5] organic-inorganic hybrid materials[6] to 2D exfoliated nanosheets.[7–9] They can present various interesting properties for instance in the field of energy (fuel cells, artificial photosynthesis, photovoltaics, batteries…) or in nanoelectronics (high-κ dielectrics, ferroelectrics, multiferroics…).[4] Among ion-exchangeable layered metal oxides, layered perovskites, Dion-Jacobson, Ruddlesden-Popper and Aurivillius phases, have probably been the most widely studied.[1,10–15]

One of the teams involved in this project has been interested for several years in the synthesis and characterization of lamellar hybrid materials, notably layered oxides and hydroxides essentially for their magnetic, optical or electrochemical properties.[16,17] Therefore this team has developed new synthetic strategies for functionalizing such layered materials.[18–21] Very recently, several reports by us and others have underlined the considerable progress offered by microwave activation for the functionalization of such layered perovskites, notably in terms of speed of the reactions.[6,19,22–25] In addition, apart from classical insertion or grafting reactions,[22–24] microwave-assisted post-synthesis modification[26] and exfoliation[27,28] have also been reported. On the other hand, the other team involved in this project has its expertise in synthesizing and characterizing active fluorophores such as curcuminoid that can be used for bio-imaging,[29] organic photovoltaic[30] and organic light emitting diodes.[31]

In this respect, we propose during this M1 internship to take advantage of the joint experience of those two teams to design new persistently luminescent materials. Indeed, such materials are receiving growing attention, but to the best of our knowledge layered oxides have not been explored yet for this purpose, contrarily to Layered Double Hydroxides or Metal Organic Frameworks,[32] despite of the advantages they offer, such as great thermal and chemical stability. More specifically, in this project, while the inorganic hosts will consist in layered tantalate, layered niobiate and layered titanates, the organic guest will be based on curcuminoid dye. Therefore, the guest molecules will be designed to favor persistent luminescence, and to be able to undergo insertion grafting reactions (*i.e.* being chemically stable in mild conditions and bearing an anchoring group).

(1) Schaak, R. E.; Mallouk, T. E. Perovskites by Design: A Toolbox of Solid-State Reactions. *Chem. Mater.* **2002**, *14* (4), 1455–1471. https://doi.org/10.1021/cm010689m.

(2) Sanjaya Ranmohotti, K. G.; Josepha, E.; Choi, J.; Zhang, J.; Wiley, J. B. Topochemical Manipulation of Perovskites: Low-Temperature Reaction Strategies for Directing Structure and Properties. *Adv. Mater.* **2011**, *23* (4), 442–460. https://doi.org/10.1002/adma.201002274.

(3) Gopalakrishnan, J.; Sivakumar, T.; Ramesha, K.; Thangadurai, V.; Subbanna, G. N. Transformations of Ruddlesden−Popper Oxides to New Layered Perovskite Oxides by Metathesis Reactions. *J. Am. Chem. Soc.* **2000**, *122* (26), 6237–6241. https://doi.org/10.1021/ja9914644.

(4) Uppuluri, R.; Gupta, A. S.; Rosas, A. S.; Mallouk, T. E. Soft Chemistry of Ion-Exchangeable Layered Metal Oxides. *Chem. Soc. Rev.* **2018**, *47* (7), 2401–2430. https://doi.org/10.1039/C7CS00290D.

(5) Montasserasadi, D.; Mohanty, D.; Huq, A.; Heroux, L.; Payzant, E. A.; Wiley, J. B. Topochemical Synthesis of Alkali-Metal Hydroxide Layers within Double- and Triple-Layered Perovskites. *Inorg. Chem.* **2014**, *53* (3), 1773–1778. https://doi.org/10.1021/ic402957c.

(6) Akbarian-Tefaghi, S.; Wiley, J. B. Microwave-Assisted Routes for Rapid and Efficient Modification of Layered Perovskites. *Dalton Trans.* **2018**, *47* (9), 2917–2924. https://doi.org/10.1039/C7DT03865H.

(7) Wang, L.; Sasaki, T. Titanium Oxide Nanosheets: Graphene Analogues with Versatile Functionalities. *Chem. Rev.* **2014**, *114* (19), 9455–9486. https://doi.org/10.1021/cr400627u.

(8) Li, B.-W.; Osada, M.; Ebina, Y.; Ueda, S.; Sasaki, T. Coexistence of Magnetic Order and Ferroelectricity at 2D Nanosheet Interfaces. *J. Am. Chem. Soc.* **2016**, *138* (24), 7621–7625. https://doi.org/10.1021/jacs.6b02722.

(9) Ma, R.; Sasaki, T. Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites. *Adv. Mater.* **2010**, *22* (45), 5082–5104. https://doi.org/10.1002/adma.201001722.

(10) Tahara, S.; Ichikawa, T.; Kajiwara, G.; Sugahara, Y. Reactivity of the Ruddlesden−Popper Phase H2La2Ti3O10 with Organic Compounds: Intercalation and Grafting Reactions. *Chem. Mater.* **2007**, *19* (9), 2352–2358. https://doi.org/10.1021/cm0623662.

(11) Takahashi, S.; Nakato, T.; Hayashi, S.; Sugahara, Y.; Kuroda, K. Formation of Methoxy-Modified Interlayer Surface via the Reaction between Methanol and Layered Perovskite HLaNb2O7.Cntdot.xH2O. *Inorg. Chem.* **1995**, *34* (20), 5065–5069. https://doi.org/10.1021/ic00124a023.

(12) Takeda, Y.; Momma, T.; Osaka, T.; Kuroda, K.; Sugahara, Y. Organic Derivatives of the Layered Perovskite HLaNb2O7·xH2O with Polyether Chains on the Interlayer Surface: Characterization, Intercalation of LiClO4, and Ionic Conductivity. *J. Mater. Chem.* **2008**, *18* (30), 3581–3587. https://doi.org/10.1039/B802003E.

(13) Suzuki, H.; Notsu, K.; Takeda, Y.; Sugimoto, W.; Sugahara, Y. Reactions of Alkoxyl Derivatives of a Layered Perovskite with Alcohols: Substitution Reactions on the Interlayer Surface of a Layered Perovskite. *Chem. Mater.* **2003**, *15* (3), 636–641. https://doi.org/10.1021/cm0200902.

(14) Wang, C.; Tang, K.; Wang, D.; Liu, Z.; Wang, L.; Zhu, Y.; Qian, Y. A New Carbon Intercalated Compound of Dion–Jacobson Phase HLaNb2O7. *J. Mater. Chem.* **2012**, *22* (22), 11086–11092. https://doi.org/10.1039/C2JM14902H.

(15) Shimada, A.; Yoneyama, Y.; Tahara, S.; Mutin, P. H.; Sugahara, Y. Interlayer Surface Modification of the Protonated Ion-Exchangeable Layered Perovskite HLaNb2O7•xH2O with Organophosphonic Acids. *Chem. Mater.* **2009**, *21* (18), 4155–4162. https://doi.org/10.1021/cm900228c.

(16) Rogez, G.; Massobrio, C.; Rabu, P.; Drillon, M. Layered Hydroxide Hybrid Nanostructures: A Route to Multifunctionality. *Chem. Soc. Rev.* **2011**, *40* (2), 1031–1058. https://doi.org/10.1039/C0CS00159G.

(17) Bourzami, R.; Eyele-Mezui, S.; Delahaye, E.; Drillon, M.; Rabu, P.; Parizel, N.; Choua, S.; Turek, P.; Rogez, G. New Metal Phthalocyanines/Metal Simple Hydroxide Multilayers: Experimental Evidence of Dipolar Field-Driven Magnetic Behavior. *Inorg. Chem.* **2014**, *53* (2), 1184–1194. https://doi.org/10.1021/ic4027688.

(18) Wang, Y.; Delahaye, E.; Leuvrey, C.; Leroux, F.; Rabu, P.; Rogez, G. Efficient Microwave-Assisted Functionalization of the Aurivillius-Phase Bi2SrTa2O9. *Inorg. Chem.* **2016**, *55* (8), 4039–4046. https://doi.org/10.1021/acs.inorgchem.6b00338.

(19) Wang, Y.; Nikolopoulou, M.; Delahaye, E.; Leuvrey, C.; Leroux, F.; Rabu, P.; Rogez, G. Microwave-Assisted Functionalization of the Aurivillius Phase Bi2SrTa2O9: Diol Grafting and Amine Insertion vs. Alcohol Grafting. *Chem. Sci.* **2018**, *9* (35), 7104–7114. https://doi.org/10.1039/C8SC01754A.

(20) Palamarciuc, O.; Delahaye, E.; Rabu, P.; Rogez, G. Microwave-Assisted Post-Synthesis Modification of Layered Simple Hydroxides. *New J. Chem.* **2014**, *38* (5), 2016–2023. https://doi.org/10.1039/C3NJ01231J.

(21) Wang, Y.; Delahaye, E.; Leuvrey, C.; Leroux, F.; Rabu, P.; Rogez, G. Post-Synthesis Modification of the Aurivillius Phase Bi2SrTa2O9 via In Situ Microwave-Assisted "Click Reaction." *Inorg. Chem.* **2016**, *55* (19), 9790–9797. https://doi.org/10.1021/acs.inorgchem.6b01600.

(22) Boykin, J. R.; Smith, L. J. Rapid Microwave-Assisted Grafting of Layered Perovskites with n-Alcohols. *Inorg. Chem.* **2015**, *54* (9), 4177–4179. https://doi.org/10.1021/ic503001w.

(23) Akbarian-Tefaghi, S.; Teixeira Veiga, E.; Amand, G.; Wiley, J. B. Rapid Topochemical Modification of Layered Perovskites via Microwave Reactions. *Inorg. Chem.* **2016**, *55* (4), 1604–1612. https://doi.org/10.1021/acs.inorgchem.5b02514.

(24) Wang, Y.; Delahaye, E.; Leuvrey, C.; Leroux, F.; Rabu, P.; Rogez, G. Efficient Microwave-Assisted Functionalization of the Aurivillius-Phase Bi2SrTa2O9. *Inorg. Chem.* **2016**, *55* (8), 4039–4046. https://doi.org/10.1021/acs.inorgchem.6b00338.

(25) Wang, Y.; Leuvrey, C.; Delahaye, E.; Leroux, F.; Rabu, P.; Taviot-Guého, C.; Rogez, G. Tuning the Organization of the Interlayer Organic Moiety in a Hybrid Layered Perovskite. *J. Solid State Chem.* **2019**, *269*, 532–539. https://doi.org/10.1016/j.jssc.2018.10.034.

(26) Wang, Y.; Delahaye, E.; Leuvrey, C.; Leroux, F.; Rabu, P.; Rogez, G. Post-Synthesis Modification of the Aurivillius Phase Bi2SrTa2O9 via In Situ Microwave-Assisted “Click Reaction.” *Inorg. Chem.* **2016**, *55* (19), 9790–9797. https://doi.org/10.1021/acs.inorgchem.6b01600.

(27) Akbarian-Tefaghi, S.; Rostamzadeh, T.; Brown, T. T.; Davis-Wheeler, C.; Wiley, J. B. Rapid Exfoliation and Surface Tailoring of Perovskite Nanosheets via Microwave-Assisted Reactions. *ChemNanoMat* **2017**, *3* (8), 538–550. https://doi.org/10.1002/cnma.201700124.

(28) Payet, F.; Bouillet, C.; Leroux, F.; Leuvrey, C.; Rabu, P.; Schosseler, F.; Taviot-Guého, C.; Rogez, G. Fast and Efficient Shear-Force Assisted Production of Covalently Functionalized Oxide Nanosheets. *Journal of Colloid and Interface Science* **2022**, *607*, 621–632. https://doi.org/10.1016/j.jcis.2021.08.213.

(29) K. Kamada, T. Namikawa, S. Senatore, C. Matthews, P.-F. Lenne, O. Maury, C. Andraud, M. Ponce-Vargas, B. Le Guennic, D. Jacquemin, P. Agbo, D. D. An, S. S. Gauny, X. Liu, R. J. Abergel, F. Fages, A. D’Aléo *Chemistry a European Journal* **2016**, *22*, 5219–5232. Boron Difluoride Curcuminoid Fluorophores with Enhanced Two-Photon Excited Fluorescence Emission and Versatile Living-Cell. https://doi.org/10.1002/chem.201504903

(30) F. Archet, D. Yao, S. Chambon, M. Abbas, A. D’Aléo, G. Canard, M. Ponce-Vargas, E. Zaborova, B. Le Guennic, G. Wantz and F. Fages *ACS Energy Letters*, **2017**, *2*, 1303–1307. Synthesis of Bioinspired Curcuminoid Small Molecules for Solution-Processed Organic Solar Cells with High Open-Circuit Voltage. https://doi.org/10.1021/acsenergylett.7b00157

(31) D.-H. Kim, A. D’Aléo, X.-K. Chen, A.S.D. Sandanayaka, D. Yao, L. Zhao, T. Komino, E. Zaborova, G. Canard, Y. Tsuchiya, E.Y. Choi, J.W. Wu, F. Fages, J.-L. Brédas, J.-C. Ribierre and C. Adachi Nature Photonics **2018**, *12*, 98-104. High-efficiency electroluminescence and amplified spontaneous emission from a thermally-activated delayed fluorescent near infrared emitter. https://doi.org/10.1038/s41566-017-0087-y

(32) Gao, R.; Kodaimati, M. S.; Yan, D. Recent Advances in Persistent Luminescence Based on Molecular Hybrid Materials. *Chem. Soc. Rev.* **2021**, *50* (9), 5564–5589. https://doi.org/10.1039/D0CS01463J.